

§Appl. No. 10/666,523
Amdt. dated August 28, 2008
Reply to Office Action of May 28, 2008

REMARKS

Claim Amendments:

Claim 43 has been amended to include the limitations found in claims 31, 32, 33 and 34. These limitations have been considered and discussed in paragraphs 13-16 of the final office action such that this amendment does not raise new issues after final.

Objection to Claim 44

Claim 44 has been objected to as allegedly presenting new matter into the disclosure by performing dehydrogenation of the distillation raffinate product without the addition of steam. The examiner finds that page 15, lines 11-17, does not support this limitation in claim 44 in that it allegedly recites only a catalyst composition. Applicants agree the disclosure within this lines focuses on the catalyst but this language is part of a broader description of the conditions for dehydrogenating ethylbenzene within lines 6-17 and steam is not mentioned. Steam is also not mentioned in describing the operating conditions for the unit for dehydrogenating ethylbenzene to styrene used in Example 1 (see page 19, line 20 through page 20 , line 5). Methods for dehydrogenation ethylbenzene to styrene with CO₂ were known to those skilled in the art at the time of this invention (See Attachment A, Ikenaga et al, Dehydrogenation of Ethylbenzene with Carbon Dioxide Using Activated Carbon Supported Catalyst, Abstract, (2/9/2000)). Therefore, Applicants maintain claim 44 does not present new matter

Rejections Under 35 U.S.C. §103:

Applicants maintain the combined teachings of the cited references do not show all the elements of the processes claimed as discussed below.

§Appl. No. 10/666,523
Amdt. dated August 28, 2008
Reply to Office Action of May 28, 2008

Dehydrogenation of minor amounts of ethylbenzene

One element that is missing from the combined teachings of the cited references is the step of dehydrogenating a mixture of ethylbenzene and xylenes (metaxylene and orthoxylene) to obtain styrene wherein the ethylbenzene is present in a “minor” amount yet at least 50 % is converted to styrene.

Magne-Drisch does not mention the dehydrogenation of ethyl benzene and provides no guidance in performing such a step.

Lee compares the performance of a catalyst formulation containing an alkali promoter and a minor amount of combined chlorine to a conventional dehydrogenation catalyst using ethylbenzene as a feed at purity levels ranging from 99.5 and 99.7%.

The dehydrogenation step involved in the methods of the claimed invention is very different from those disclosed by Lee. Purity levels of 99.5 and 99.7% ethyl benzene are not a “minor” amount and one skilled in the art has no reason to predict the dehydrogenation of minor amounts of ethylbenzene would achieve 50 % conversion based on the teachings of Lee. By processing only pure ethylbenzene, Lee provides no guidance or expectations as to the outcome of processing mixtures of xylenes with ethylbenzene present in a minor amount.

The examiner alleges that, “It is known to those skilled in the art that in the commercial practice the feed for dehydrogenation could comprise ethyl benzene and other components as claimed by the applicant.” The examiner has not provided evidence of this knowledge. Disclosures regarding the dehydrogenation of ethylbenzene which are contemporary with the disclosure of Lee (US Patents 3,308,179 (1967) and US 2,959,626 (1960), Attachments B and C) teach the importance of using high purity ethylbenzene in dehydrogenation processes to obtain polymerization grade styrene. The examiner has not presented any evidence to suggest those skilled art at the time of applicant’s invention thought differently. In addition, in response to applicant’s arguments that the references provide no guidance as to whether other compounds compete with ethylbenzene or react with the styrene product, the examiner acknowledged the 99% pure ethyl benzene reaction product contains

§Appl. No. 10/666,523
Amdt. dated August 28, 2008
Reply to Office Action of May 28, 2008

contains “no other compounds in substantial amount to provide competing reactions and reduce the yield of styrene.” No evidence has been presented to refute these arguments. In the absence of such evidence, the rejection of claims 21-37 and 39-47 under 35 USC § 103(a) is unsupported and should be withdrawn.

Dehydrogenation of products with 7 wt% of ethylbenzene or less –Claim 42

In the embodiments defined in Claim 42, the product containing metaxylene, orthoxylene and ethylbenzene which is dehydrogenated contains less than 7wt % ethylbenzene. The examiner alleges Magne-Dirsch mentions, the quantity of ethylbenzene can be “very little.” It is not clear from the record when the quantity of ethylbenzene can be “very little” in the processes of Magne-Dirsch. However, since Magne-Dirsch does not even mention dehydrogenation of ethyl benzene, any quantification of ethylbenzene in the processes disclosed provides no direction or guidance to lead one skilled in the art to the embodiments defined in claim 42.

Dehydrogenation without steam-Claim 44

As discussed in the last response, Lee discloses dehydrogenation processes that employ steam. The embodiments of claim 44 exclude the use of steam. These arguments were not considered in that the examiner alleged this limitation presented new matter. Applicants have cited other portions of the disclosure with the specification which show that steam was not required.

Dehydrogenation Catalyst does include Iron oxide (Claim 45) or Chlorine (Claim 46)

The catalysts used by Lee are distinct from those employed in the methods of claims 45 and 46 which exclude iron oxide and chlorine, respectively. While Lee mentions that the dehydrogenation the catalysts known in the art usually contain certain metals of Groups IV and VIII of the periodic table, there is no basis to ignore the specific teachings of Lee which require iron oxide and a chlorine compound be present in the catalyst. To exclude these components from the catalyst

clearly would not be obvious in view of the teachings of Lee.

Distinct reaction mixture and separation of styrene

The process of the present invention also provides a distinct reaction product mixture of styrene, metaxylene, orthoxylene, unconverted ethylbenzene and by-products which requires separation of the styrene product. The combined teachings of the cited references do not disclose an equivalent step and therefore, provide no indication of how to separate styrene from such a reaction mixture. No evidence has been presented that the recovery of styrene from these mixtures at high purity levels of at least 99.8 % would be expected.

The examiner refers to the teachings of Magne-Dirsch regarding the separation of metaxylene, orthoxylene, and ethylbenzene as relevant to this element. However, these teachings provide no guidance with respect to the separation of styrene. The examiner combines the teachings of Lee and Magne-Dirsch finding the only difference being the sequence of steps. Such an analysis expressly ignores the feature of this invention which is the sequence of the process steps as well as the features within the steps themselves such as isolating styrene and dehydrogenating ethylbenzene within a mixture in minor amounts. No evidence has been presented suggesting it would be obvious to first dehydrogenate a mixture of ethylbenzene and xylenes followed by separation of styrene from the reaction mixture based on the combined teachings of Lee and Magne-Dirsch.

Separating styrene with a second absorption column

The embodiments of claim 22 require that the styrene be separated with a second absorption column which is simulated moving bed and the embodiments of claim 27 require the styrene be separated using a second absorption column where the adsorbent used is an X or Y zeolite. The examiner alleges the use of X or Y zeolite in the second adsorption column is functionally similar to the adsorption disclosed by Magne-Dirsch. This is not possible since applicants employ the second adsorption column to isolate styrene and not ethylbenzene. As mentioned above, the cited references

§Appl. No. 10/666,523
Amdt. dated August 28, 2008
Reply to Office Action of May 28, 2008

do not even mention isolating styrene, let alone using an adsorption column to do so. In that neither reference shows the separation of styrene, the cited references do not show the elements of these claims and the rejection of these claims under 35 USC §103(a) should be withdrawn.

Obviousness-type Double Patenting:

The methods claimed herein are clearly patentably distinct from the methods defined in claims 1-20 of U.S. Patent 6,841,714 such that there is no basis for the rejection under the doctrine of obviousness type double patenting. The claims of U.S. Patent 6,841,714 do not include the dehydrogenation step or the isolation of styrene required of the methods claimed herein and no evidence has been presented to show or suggest it would be obvious for one skilled in the art to do so.

It is alleged that based on prior art such as Magne-Dirsch and Lee it would be obvious to prepare styrene from the ethylbenzene produced by the methods of US 6,841,714. While the use of ethylbenzene to prepare styrene was known, it was not known that the ethylbenzene could be used without the isolation steps of Magne-Dirsch such that the subject matter claimed herein is not obvious in view of the methods claimed within US 6,841,714.

§Appl. No. 10/666,523
Amdt. dated August 28, 2008
Reply to Office Action of May 28, 2008

Based on the above remarks, Applicants submit that all pending claims are in a form suitable for allowance and patentable over the cited references. Therefore, withdrawal of the rejections and allowance of these claims are earnestly solicited.

The Commissioner is hereby authorized to charge any fees associated with this response or credit any overpayment to Deposit Account No. 13-3402.

Respectfully submitted,

/Richard J. Traverso.


Richard J. Traverso, Reg. No. 30,595

Attorney/Agent for Applicant(s)

MILLEN, WHITE, ZELANO
& BRANIGAN, P.C.
Arlington Courthouse Plaza 1, Suite 1400
2200 Clarendon Boulevard
Arlington, Virginia 22201
Telephone: (703) 243-6333
Facsimile: (703) 243-6410

Attorney Docket No.: PET-2102

Date: August 28, 2008


[Table of Contents](#) | [Journal Home Page](#) | [Search the Journals](#)
Ind. Eng. Chem. Res., 39 (5), 1228 -1234, 2000. 10.1021/ie990426q S0888-5885(99)00426-1

Web Release Date: March 28, 2000

Copyright © 2000 American Chemical Society

Full Text HTML
Download Citation
Purchase Article

Dehydrogenation of Ethylbenzene with Carbon Dioxide Using Activated Carbon-Supported Catalysts

Na-oki Ikenaga,* Tadatoshi Tsuruda, Kazuhiro Senma, Takanori Yamaguchi, Yoshihiro Sakurai, and Toshimitsu Suzuki

Department of Chemical Engineering, Faculty of Engineering, Kansai University, Suita, Osaka 564-8680, Japan

Received for review June 15, 1999

Revised manuscript received December 1, 1999

Accepted February 9, 2000

Abstract:

Dehydrogenation of ethylbenzene to styrene under excess carbon dioxide flow was carried out over activated carbon-supported metal oxide catalysts (Cr, Mn, Co, Ni, Mo, Ru, La, and Ce) at 823 K and $W/F = 35$ g of catalyst·h/mol. The highest yield of styrene (about 40%) with selectivity of above 80% was obtained using activated carbon-supported chromium oxide (Cr/AC) and cerium oxide (Ce/AC) catalysts. The initial activities of the Cr/AC and Ce/AC catalysts were comparable to that of an iron-loaded activated carbon catalyst reported previously. Only chromium(III) oxide and cerium(IV) oxide were detected by X-ray diffraction before and after reactions at higher loading levels, and these species might have been active forms. However, a reduced chromium oxide species was detected by X-ray photoelectron spectroscopy after reaction under argon. In addition to the produced styrene, equivalent amounts of carbon monoxide and water were formed. These results suggest that the dehydrogenation of ethylbenzene to styrene proceeds via two reaction paths. One is the simple dehydrogenation and an oxidation reaction of hydrogen formed with carbon dioxide. The other is the oxidative dehydrogenation of ethylbenzene through the redox cycle of chromium(III) oxide.

[Download the full text: PDF | HTML](#)
Attachment A

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,308,179

March 7, 1967

John A. Scott

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 75, for "1175° C." read -- 1175° F. --.

Signed and sealed this 7th day of November 1967.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents

Attachment B

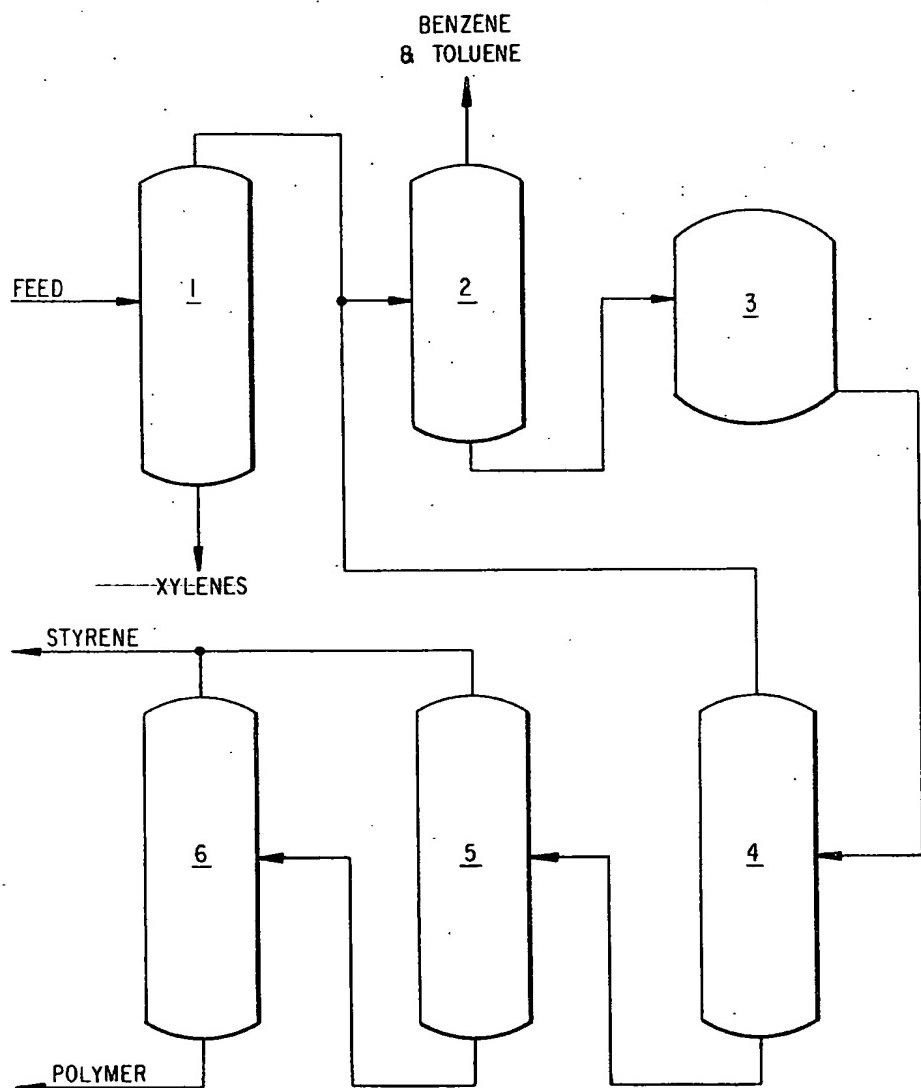
March 7, 1967

J. A. SCOTT

3,308,179

PROCESS FOR DEHYDROGENATION OF ETHYLBENZENE

Filed Jan. 31, 1964



INVENTOR
JOHN A. SCOTT

BY
McLean & Bousted
ATTORNEYS

United States Patent Office

3,308,179

Patented Mar. 7, 1967

1

3,308,179

PROCESS FOR DEHYDROGENATION OF ETHYLBENZENE

John A. Scott, New York, N.Y., assignor, by mesne assignments, to Sinclair Research, Inc., New York, N.Y., a corporation of Delaware

Filed Jan. 31, 1964, Ser. No. 341,535

7 Claims. (Cl. 260—669)

This invention relates to the production of high purity styrene by dehydrogenation in a system into which is fed a relatively impure ethylbenzene stream. According to the process of this invention, high purity styrene, for instance, having a purity of at least 99 weight percent or even at least 99.5%, based on C₈ aromatic hydrocarbons is produced in a catalytic dehydrogenation process using an ethylbenzene feedstock of a purity of 95 to 98.5 weight percent, preferably 96 to 97.5%.

The catalytic dehydrogenation of ethylbenzene to form styrene is well known in the art. For polymerization grade styrene, a purity of at least 99.5% is usually required. Styrene containing more than about 1% of a stable hydrocarbon boiling in the C₈ aromatics range is generally useless for normal commercial polymer purposes. Thus in the production of commercial styrene, it is very important to prevent the presence of impurities in the product. Normally the styrene-containing effluent which has been formed by dehydrogenation of feeds prepared by separation from petroleum fractions, contains both ethylbenzene as a result of incomplete dehydrogenation and xylene impurities. The ethylbenzene and xylene are normally removed overhead from the styrene product bottoms and the overhead is recycled to the dehydrogenation reactor. Thus it was considered that the making of a styrene product of given concentration permitted the presence of xylene in the feed only to the same extent since any xylene in the ethylbenzene feed would build up in the recycle stream until equilibrium is established and at this point, the amount of xylene which goes into the styrene product is equal to the amount of xylene entering as an impurity in the ethylbenzene feed. Therefore it has been considered necessary to use an ethylbenzene feed of extremely high purity, normally greater than 99.5%. See U.S. Patents Nos. 2,959,626 and 3,084,108.

The object of this invention is to prepare high purity styrene using as a starting material ethylbenzene of relatively lower purity. The object of this invention is further to make it possible to produce high purity styrene by the use of less expensive ethylbenzene feed distillation systems than heretofore required or to increase the capacity of existing systems for obtaining the ethylbenzene feed stream from aromatic petroleum fractions. For example, the amount of ethylbenzene available for dehydrogenation, and thus the amount of styrene produced may be increased by about 21% when the ethylbenzene fed to the dehydrogenation system is only 97% pure, rather than 99.5%, based on total C₈ hydrocarbons.

The process of this invention is based upon the discovery that in the system of the present invention sufficient amounts of xylenes are cracked in the dehydrogenation reactor to lower boiling impurities such as benzene and toluene. As a practical matter, all xylenes are not removed from the styrene product. Thus the amount of xylenes cracked plus the amount of xylene in the styrene product is essentially equal to the amount of xylene entering in the ethylbenzene feed, and accordingly the amount of xylenes cracked is essentially equal to the amount of xylene in the C₈ aromatic hydrocarbon feed stream minus the xylene in the styrene product.

In the process for purification of the ethylbenzene feedstock, two distillation columns are often employed. The

2

first separates the bulk of the higher boiling xylenes from ethylbenzene and the second removes the lower boiling benzene and toluene from the ethylbenzene. This sequence can be reversed; however, by removing the benzene and toluene first. A common column may be employed for distilling benzene and toluene from the feedstock and from the C₈ stream being recycled in the dehydrogenation system. In any event, according to this invention, the ethylbenzene feed to the dehydrogenation system contains 95 to 98.5%, preferably 96 to 97.5%, ethylbenzene based on the total of ethylbenzene and xylenes.

After separation, the ethylbenzene is catalytically dehydrogenated. Generally the dehydrogenation temperature should be in the range of about 1000 to 1200° F. and preferably about 1050 to 1175° F. Any suitable ethylbenzene dehydrogenation catalyst may be used. Typical dehydrogenation catalysts are commercially available catalysts which comprise 90% Fe₂O₃, 4% Cr₂O₃ and 6% K₂CO₃; or 62.5% Fe₂O₃, 2.2% Cr₂O₃ and 35.3% K₂CO₃. Other suitable catalyst compositions are as follows: 60–95% iron oxide, 4–39% potassium oxide and 1–10% chromium oxide; 5–60% cobalt oxide, 10–60% iron oxide, 4–39% potassium oxide and 1–10% chromium oxide; 50–90% iron oxide, 9–49% calcium oxide and 1–4% chromium oxide. These catalysts often consist essentially of the oxides of an iron group metal; an alkaline metal including the alkali and alkaline earth metals and chromium. The oxide form of the metals includes compounds that decompose to an oxide under the reaction or similar conditions.

The dehydrogenation may be carried out at atmospheric or elevated or reduced pressures. With pressures in the range of about 200 p.s.i.g. the hydrocarbon feed is often diluted with from about 1 to 10 volumes of steam to reduce the hydrocarbon partial pressure. The space velocity can be varied and when using a catalyst the WHSV (pounds hydrocarbon per pound of catalyst per hour) may often vary from about 0.1 to 5, preferably from 0.4 to 0.7. In general, standard dehydrogenation reactor conditions have been found satisfactory.

It has been found that the amount of xylenes cracked increases with increasing ethylbenzene conversion, and it is usually only necessary to keep the conversion of ethylbenzene high enough so that the amount of xylene cracked is about equal to the amount in the feed minus that in the styrene product. In general, the ethylbenzene conversion will be in the range of about 25 to 70%, preferably about 30 to 60%. It is desirable that the distillation column for separating the recycle stream be capable of separating xylene and ethylbenzene from styrene without a large amount of styrene going to the recycle stream in order to avoid undue polymerization of the styrene in the dehydrogenation reactor. Generally, the column should be capable of making a separation which yields a styrene product of at least 99% or even at least 99.5% purity, and preferably the column will give this product and a recycle stream of less than about 3%, preferably less than 1% styrene based on C₈ aromatics when distilling the product resulting from the dehydrogenation at about 33% ethylbenzene conversion. Such a column was used in the examples which follow. Operation according to the process of this invention results in an increased ethylbenzene feed purification column capacity of 21% when 97% rather than 99.5% ethylbenzene is used, and at the same dehydrogenation conversion level gives 21% more styrene.

The process can be more readily understood by reference to the figure showing a flow sheet of the process.

Crude ethylbenzene feed enters the primary tower 1 and is purified by removing xylenes as the bottom product and taking off ethylbenzene, xylene and lighter materials over-

head. This overhead is joined with the recycle stream from the dehydrogenation system and the combined material is passed into distillation column 2. In column 2, benzene and toluene are removed overhead and ethylbenzene and xylenes are taken as a bottom product. As an alternative mode of operation, the ethylbenzene and xylene from column 1 may by-pass the benzene-toluene separation column 2 and go directly to dehydrogenation reactor 3, especially if the overhead from column 1 is essentially devoid of benzene and toluene. The bottom product from column 2 enters the dehydrogenation reactor 3 wherein ethylbenzene is converted to styrene. The dehydrogenation reactor effluent is separated in recycle distillation column 4. The high purity styrene product is recovered as the bottom product from column 4 and the overhead stream containing styrene, xylene, ethylbenzene, benzene and toluene is recycled to column 2.

Purification of the styrene may take place in the continuous finishing distillation tower 5 which has a highly pure styrene overhead product and a styrene and poly-

styrene bottoms product and batch finishing column 6, which has a styrene overhead product and a polymer bottoms product.

The following examples illustrate the process of this invention.

Example I

An ethylbenzene feed was converted to styrene in equipment of the type described. Crude ethylbenzene feed was first separated from xylene to give a feed containing 2% xylene, based on C₈ aromatics. Benzene and toluene impurities were removed in a second distillation. The bottoms products from the benzene-toluene column were then sent to a dehydrogenation reactor containing a dehydrogenation catalyst containing approximately 90% Fe₂O₃, 4% Cr₂O₃, and 6% K₂CO₃, and from there to a recycle column which removed xylene, ethylbenzene, benzene and toluene impurities from the styrene and recycled them to the benzene-toluene column. Flow rates, stream compositions, and reactor compositions for this run are shown in Table I.

TABLE I

Composition	Flow Rates (Parts by Weight/Hr.)					
	Ethylbenzene Feed To B-T Twr. 2	Recycle and Liquid From Vent Condenser To B-T Twr. 2	Benzene-Toluene Tower 2			Vent Gas From Dehydrogenation
			Feed	OVHD To Refinery	Bottoms To Reactor	
H ₂						5.67
C ₁						1.03
C ₂						0.82
C ₃ +.....						0.11
CO ₂						10.27
Paraffin.....	0.52	1.68	2.20	0.15	2.05	
Benzene.....		6.52	6.52			
Toluene.....	13.38	15.61	23.99	23.39	5.60	
Ethylbenzene.....	163.30	146.07	309.37	4.24	305.13	
M-P Xylene.....	3.80	34.15	37.95	0.29	37.66	
Styrene.....		15.56	15.56		15.56	
Polymer.....						
Total.....	181.00	219.59	400.59	34.59	366.00	117.90

Composition	Flow Rates (Parts by Weight/Hr.)					
	Recycle Tower 4				Finishing Tower 5	
	Feed	OVHD Vapor To B-T Twr. 2 Via Vent Cond.	OVHD Liquid To B-T Twr. 2	Bottoms To Finishing Tower 5	OVHD Product	Bottoms To Batch Still 6
H ₂						
C ₁						
C ₂	0.14					
C ₃ +.....						
CO ₂						
Paraffin.....	1.68	0.41	1.08			
Benzene.....	6.52	3.80	1.95			
Toluene.....	15.61	6.74	9.97			
Ethylbenzene.....	146.17	30.00	116.39	0.10	0.10	
M-P Xylene.....	34.72	6.62	27.06	0.57	0.57	
Styrene.....	150.41	2.43	18.14	134.85	133.60	1.25
Polymer.....	1.25			1.25		1.25
Total.....	356.50	50.00	169.69	136.77	134.27	2.50

Reactor Conditions			Reactor Feed Composition	Weight Percent
Fresh Feed (parts/hr.)		168	Paraffins.....	0.56
Recycle (parts/hr.)		198	Toluene.....	1.53
Total Reactor Feed (parts/hr.)		366	Ethylbenzene.....	83.27
Total Steam to Reactor (parts/hr.)		830	M-P Xylenes.....	10.29
Steam Temp., °F		1,400	Styrene.....	4.25
Reactor Inlet, °F		1,140		
Reactor Outlet, °F		1,090	Total.....	100.00
Conversion Per Pass, Mole percent		45		
Weight Hourly Space Velocity, #/H HC/# Cat.		0.66		

¹ 8.40 parts of the vent gas are products of the water gas reaction.

Example II

The process of Example I was repeated using an ethylbenzene feed containing 4% xylene based on C₈ aromatics. Flow rates and conditions are shown in 5

reaction as said recycle stream, the conversion of ethylbenzene in said reaction being about 25 to 70% and sufficient to crack xylenes to lower boiling materials in an amount essentially equal to the amount of xylene in the C₈ aromatic hydrocarbon feed stream minus the xylene in the high purity styrene product.

TABLE II

Composition	Flow Rates (Parts by Weight/Hr.)					
	Ethylbenzene Feed		Benzene-Toluene Tower 2			Vent Gas From Dehydrogenation
	To B-T Twr. 2	Recycle and Liquid From Vent Condenser	Feed	OVHD To Refinery	Bottoms To Reactor	
H ₂						5.51
C ₁						1.16
C ₂						0.81
C ₃ +						0.16
CO ₂						12.26
Paraffin	1.31	2.02	3.33	0.88	2.44	
Benzene		7.76	7.76			
Toluene	10.00	21.63	31.63	24.51	7.92	
Ethylbenzene	171.70	133.35	305.05	0.50	304.55	
M-P Xylene	6.99	57.80	64.79	0.03	62.83	
Styrene		28.16	28.16		28.16	
Polymer						
Total	190.00	250.00	440.00	33.68	405.9	1 19.90

Composition	Flow Rates (Parts by Weight/Hr.)					
	Recycle Tower 4			Finishing Tower 5		
	Feed	OVHD Vapor	OVHD Liquid	Bottoms To Finishing Tower 5	OVHD Product	Bottoms To Batch Still 6
Feed						
To B-T Twr. 2 Via Vent Cond.						
H ₂						
C ₁						
C ₂	0.20					
C ₃ +						
CO ₂						
Paraffin	2.02	0.53	1.64			
Benzene	7.76	3.98	2.48			
Toluene	21.63	7.50	12.26			
Ethylbenzene	133.35	25.25	113.36	0.10	0.10	
M-P Xylene	57.80	9.00	45.58	0.63	0.63	
Styrene	171.45	3.74	24.68	143.29	141.53	1.76
Polymer	1.94			1.94		1.94
Total	396.15	50.00	200.00	145.96	142.26	3.70

Reactor Conditions		Reactor Feed Composition	Weight percent
Fresh Feed (parts/hr.)			
Recycle (parts/hr.)	184	Paraffins	0.50
Total Reactor Feed (parts/hr.)	222	Toluene	1.95
Total Steam to Reactor (parts/hr.)	406	Ethylbenzene	75.03
Steam Temp. ° F	909	M-P Xylenes	13.48
Steam Inlet, ° F	1,388	Styrene	6.94
Reactor Inlet, ° F	1,155	Total	100.00
Reactor Outlet, ° F	1,112		
Conversion Per Pass, Mole percent	47.9		
Weight Hourly Space Velocity, #/H HC/# Cat	0.62		

¹ 10.15 parts/hr. of the vent gas are products of the water gas reaction.

It is claimed:

1. In the process of producing styrene of at least 99% purity based on C₈ aromatic hydrocarbons from a C₈ aromatic hydrocarbon feed stream consisting essentially of xylene and 95 to 98.5% ethylbenzene based on the C₈ aromatics which consists essentially of combining said C₈ aromatic hydrocarbon with a C₈ aromatic recycle stream, dehydrogenating said combined C₈ material at a temperature of about 1000 to 1200° F. to produce styrene by dehydrogenation of ethylbenzene, removing the high purity styrene product from the reaction effluent and recycling remaining C₈ aromatic effluent to the dehydrogenation

65 2. The method of claim 1 wherein the ethylbenzene conversion is about 30 to 60% and the styrene product is at least 99.5% pure based on C₈ aromatic hydrocarbons.

3. The method of claim 2 wherein the recycle stream is separated from the styrene product in a distillation column which gives a recycle stream of less than 3% styrene when distilling the product stream resulting from the dehydrogenation at about 33% ethylbenzene conversion.

4. The process of claim 3 wherein the dehydrogenation is at a temperature of about 1050 to 1175° C.

5. The method of claim 2 wherein the dehydrogenation is conducted in the presence of a catalytic amount of a catalyst consisting essentially of Fe_2O_3 , Cr_2O_3 and K_2CO_3 .

6. The process of claim 5 wherein the C_8 aromatic hydrocarbon feed contains 96 to 97.5% ethylbenzene based on C_8 aromatics.

7. The method of claim 1 wherein said xylene comprises a mixture of meta and para xylenes.

References Cited by the Examiner

UNITED STATES PATENTS

2,376,709	5/1945	Mattox	-----	260—669
2,963,518	12/1960	Amos et al.	-----	260—672
3,093,694	6/1963	Soderquist et al.	-----	260—669

DELBERT E. GANTZ, Primary Examiner.

C. R. DAVIS, Assistant Examiner.

Attachment C

Nov. 8, 1960

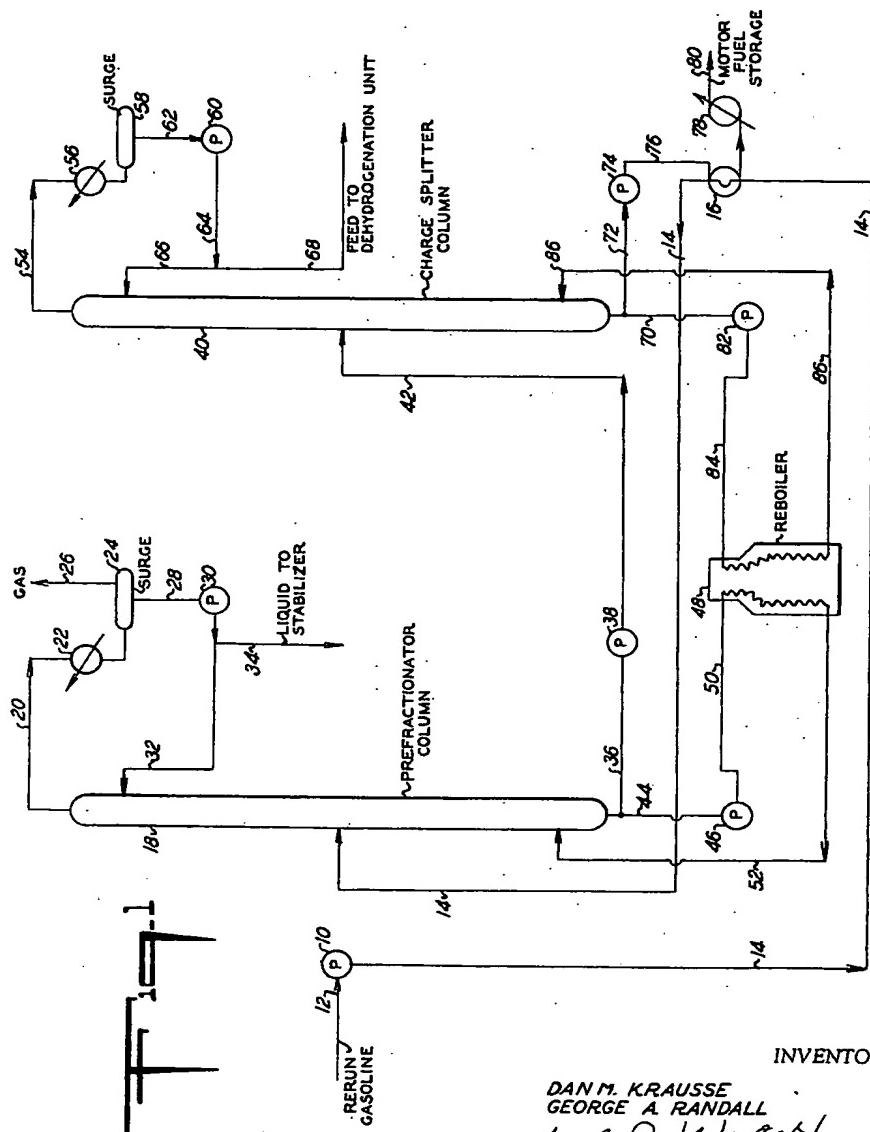
D. M. KRAUSSE ET AL

2,959,626

PROCESS FOR THE PRODUCTION OF STYRENE-GRADE ETHYL BENZENE

Filed July 15, 1957

5 Sheets-Sheet 1



INVENTOR

DAN M. KRAUSSE
GEORGE A. RANDALL

BY

Sol B. Wiegert

ATTORNEY

Nov. 8, 1960

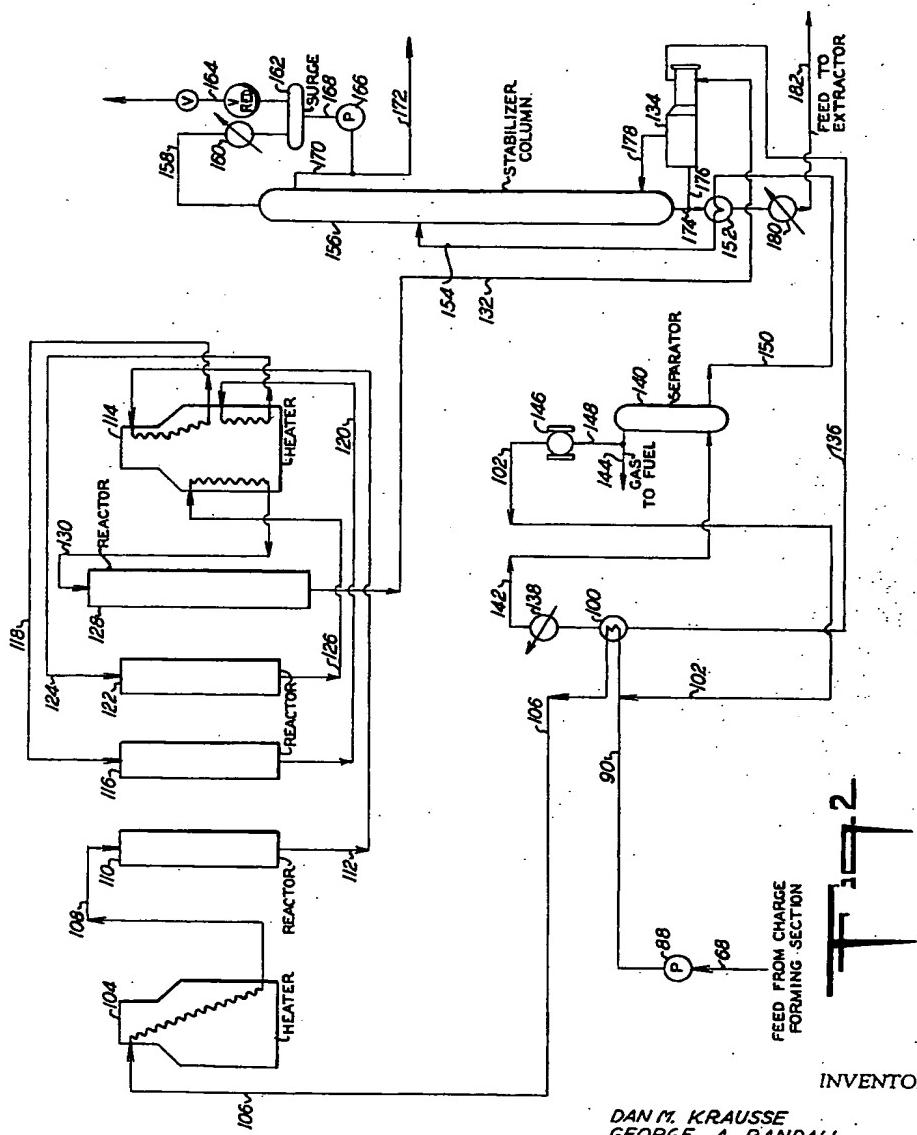
D. M. KRAUSSE ET AL

2,959,626

PROCESS FOR THE PRODUCTION OF STYRENE-GRADE ETHYL BENZENE

Filed July 15, 1957

5 Sheets-Sheet 2



ATTORNEY

Nov. 8, 1960

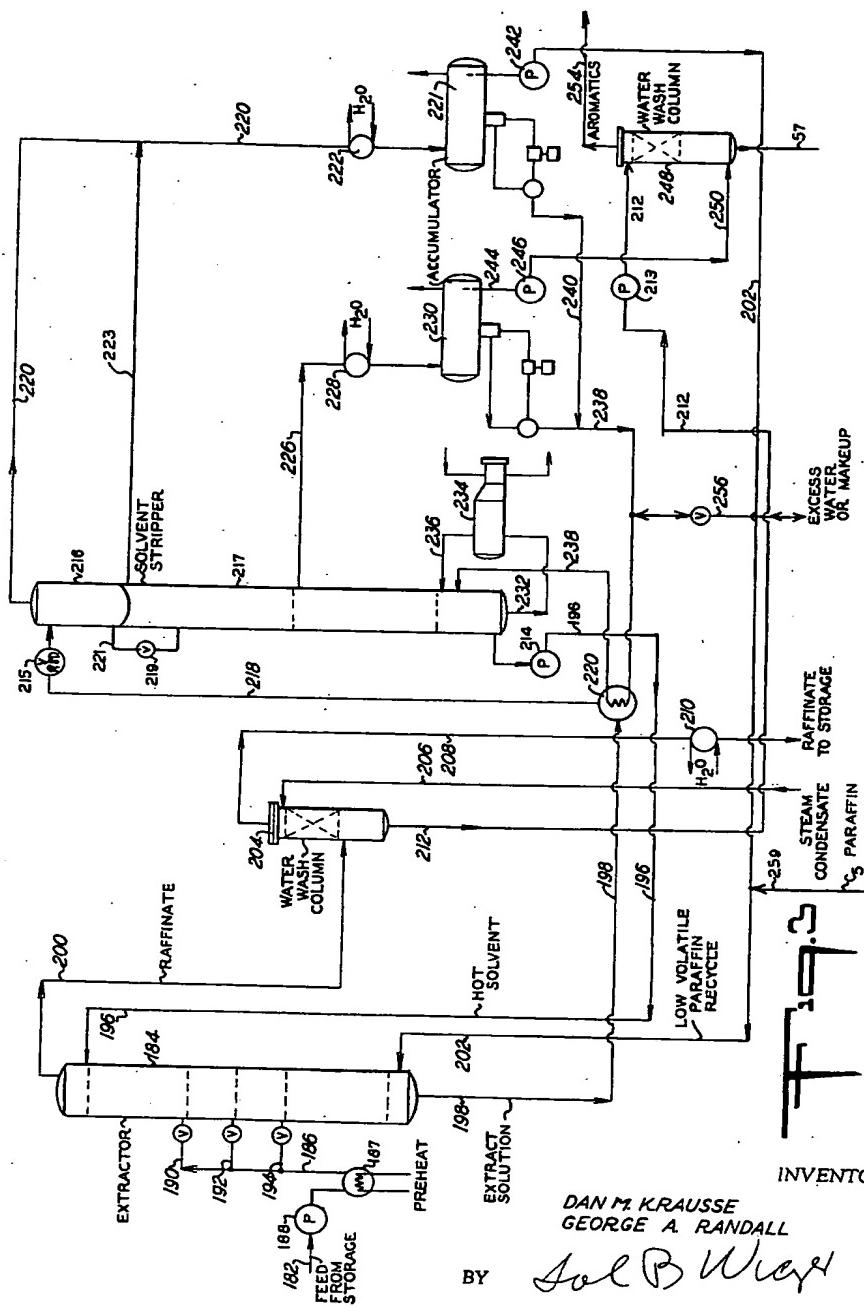
D. M. KRAUSSE ET AL.

2,959,626

PROCESS FOR THE PRODUCTION OF STYRENE-GRADE ETHYL BENZENE

Filed July 15, 1957

5 Sheets-Sheet 3



Nov. 8, 1960

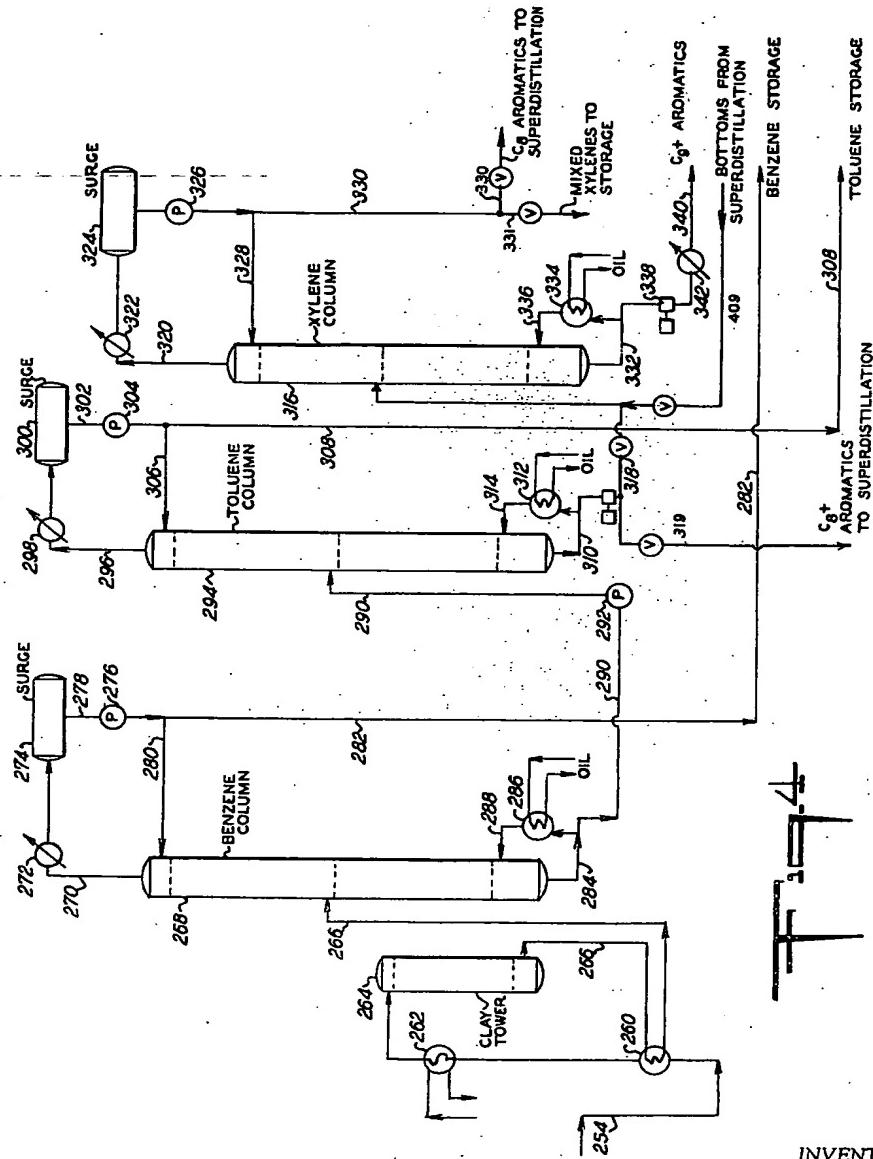
D. M. KRAUSSE ET AL

2,959,626

PROCESS FOR THE PRODUCTION OF STYRENE-GRADE ETHYL BENZENE

Filed July 15, 1957

5 Sheets-Sheet 4



INVENTOR

DAN M. KRAUSSE
GEORGE A. RANDALL

BY Sol B. Weyl

ATTORNEY

Nov. 8, 1960

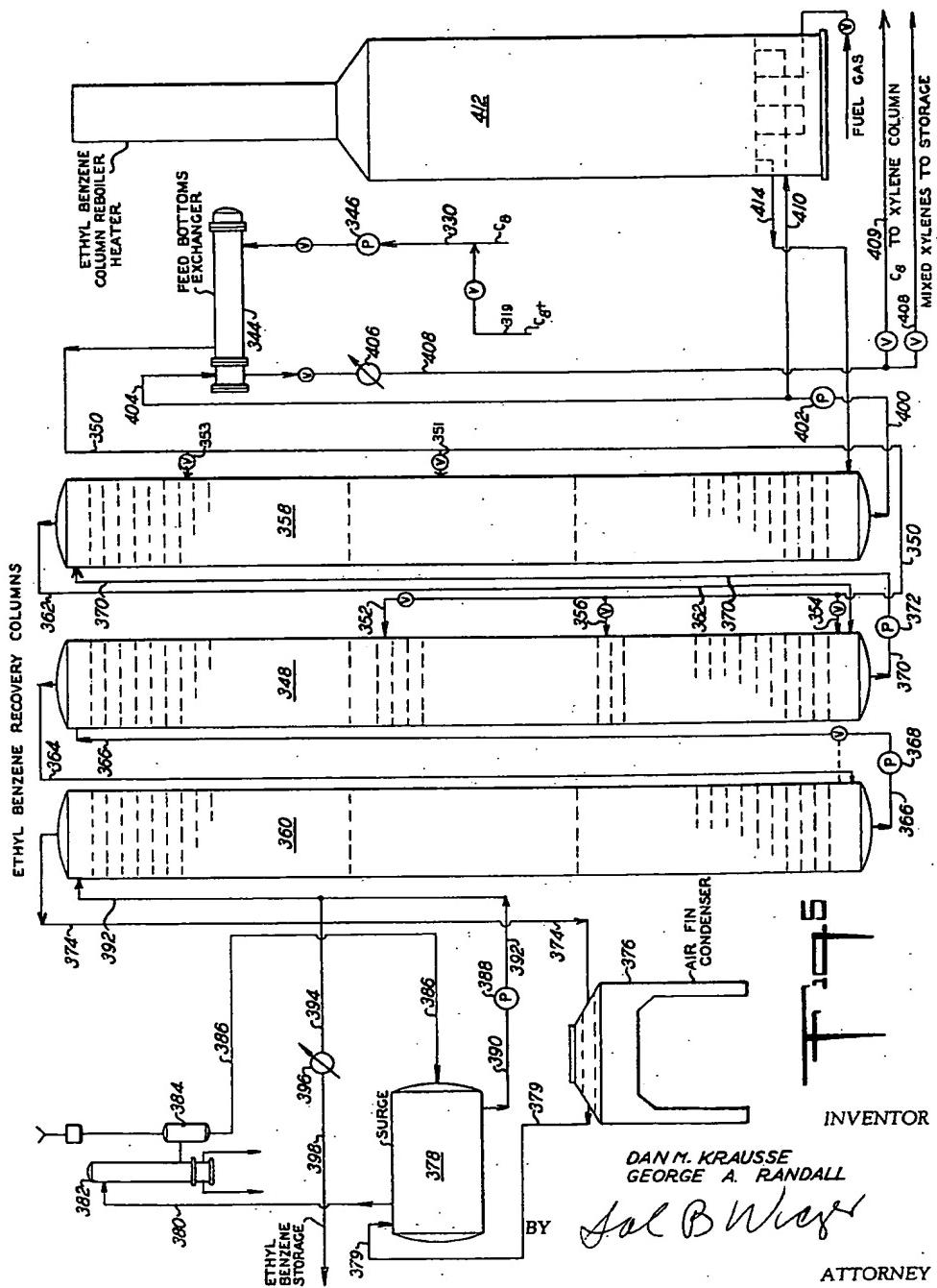
D. M. KRAUSSE ET AL

2,959,626

PROCESS FOR THE PRODUCTION OF STYRENE-GRADE ETHYL BENZENE

Filed July 15, 1957

5 Sheets-Sheet 5



United States Patent Office

2,959,626

Patented Nov. 8, 1960

1

2,959,626

PROCESS FOR THE PRODUCTION OF STYRENE- GRADE ETHYL BENZENE

Dan M. Krausse, Big Spring, Tex., and George A. Randall, Cambridge, Mass., assignors to Cosden Petroleum Corporation, Big Spring, Tex., a corporation of Delaware

Filed July 15, 1957, Ser. No. 672,053

15 Claims. (Cl. 260—674)

This invention relates to a method for producing ethylbenzene in a degree of purity suitable for dehydrogenation to styrene. As a useful dehydrogenation stock for styrene production, the ethylbenzene hereof contains less than 1 volume percent of stable hydrocarbon impurity boiling in the C₈ aromatic hydrocarbon range, a range of about 130 to 140° C.

More particularly, the present invention provides a method and apparatus by which ethylbenzene may be superdistilled from a C₈ aromatics mixture in at least that degree of purity.

The invention also provides a method of producing a C₈ aromatics fraction mixture, containing less than 0.3% of non-aromatic hydrocarbon and comprising a useful charging stock for superdistillation to recover said ethylbenzene from a naphtha containing recoverable quantities of C₈ aromatics.

The invention further provides superdistillation apparatus comprising a plurality of two or more columns to effect the distillation of a C₈ aromatics fraction from which substantially pure ethylbenzene may be recovered using at least 150 plates or stages, and preferably from 200 to 400 plates or stages; and a critical distillation method of operating such apparatus including a reflux ratio exceeding 40:1 and preferably 60 to 150:1, whereby the ethylbenzene separated has a purity exceeding 99% for styrene production, and practically may exceed 99.995%.

In the production of styrene from ethylbenzene containing more than 1% of impurity by catalytic dehydrogenation, such impurity, if it is not decomposed during the reaction to components of remote boiling point and if it boils in the neighborhood of styrene or ethylbenzene, tends to prevent separation of styrene of adequate purity from the reaction products. A styrene produced from ethylbenzene containing more than about 1% of a stable hydrocarbon boiling in the C₈ aromatics range, such as 130–140° C., is useless for usual commercial purposes. If the ethylbenzene contains less than about 1% but more than 0.4% of such impurities, the styrene produced therefrom is useful for preparing synthetic rubber such as GR-S, but not commercially acceptable polystyrene polymer. For the latter purpose the ethylbenzene must contain less than 0.4% impurity. Thus, for commercial purposes, only styrene containing less than 0.4% is useful for direct polymerization to colorless plastic polystyrene, and that grade of styrene produced from such high purity ethylbenzene is known as polymer grade styrene. Styrene produced from ethylbenzene containing

2

less than about 1% but more than 0.4% of stable hydrocarbon impurity, is known as rubber grade styrene.

The ethylbenzene produced by the present method has less than 1% of stable hydrocarbon impurity boiling in the C₈ aromatics range, such as from 130 to 140° C., and may be produced by the present method with impurities less than detectable, that is, ethylbenzene containing less than .005% impurity.

As a first step of this method, a C₈ aromatics mixture 10 is obtained which contains less than 0.3% of non-aromatic hydrocarbon boiling in the C₈ aromatics range.

As a second step, this substantially pure C₈ aromatics mixture is superdistilled in a column comprising at least 150 distillation plates or stages, preferably 200 to 400 plates or stages at a reflux ratio exceeding about 40:1, preferably in the range of 60 to 150:1. The term reflux ratio as used herein is the ratio of reflux volume to net overhead product volume.

As a further feature of this invention, stable non-aromatic hydrocarbon components usually occurring with a C₈ aromatics extract fraction are displaced during the extraction of naphthas containing an extractable quantity of ethylbenzene by substituting lower boiling, usually non-aromatic hydrocarbon, for the higher boiling non-aromatic hydrocarbon components contained in the aromatic extract, thereby allowing production of a C₈ aromatics fraction of substantially pure aromatic components, and in any case, a C₈ aromatics fraction which critically contains less than 0.3% of stable non-aromatic hydrocarbon.

According to a preferred practice of this invention, a highly naphthenic naphtha feed stock is aromatized by catalytic dehydrogenation to produce a 40–60% aromatics yield, of which the C₈ fraction contains a recoverable quantity, usually more than 10% of ethylbenzene, and we averaged, according to our preferred procedure, about 27 to 34% of ethylbenzene in our C₈ aromatics fraction.

Ethylbenzene, prior to the present invention, was produced commercially by alkylation of benzene with ethylene. This catalytic alkylation is an expensive extra step in petroleum conversion to first form the pure benzene and ethylene and then convert them to ethylbenzene. The method of this invention distinguishes that common practice in completely avoiding this catalytic synthetic method by procedures, which in most economical aspect, are applied directly to raw petroleum naphthas first to form large quantities of ethylbenzene therein and then to isolate it from other hydrocarbon components.

It is known in the art that usual conversion of petroleum naphthas, particularly such as contain aromatics will, along with the benzene, toluene and xylene, contain some ethylbenzene. In many naphthas produced by petroleum conversion the aromatic content will vary widely and the ethylbenzene content thereof may vary slightly with the character of the raw naphtha feed stock, but the C₈ aromatic fractions separated therefrom average only about 11% of ethylbenzene.

The boiling point of ethylbenzene is so close to that of the xylene isomers contained in the C₈ fraction that separation of the mixture even by very fine distillation to obtain an ethylbenzene concentrate in sufficient purity to obtain an ethylbenzene of dehydrogenation quality to produce styrene, has not heretofore been possible. For

instance, in this ethylbenzene dehydrogenation, the unconverted ethylbenzene must be separated from the styrene produced, usually in less than 50% yield per pass, by distillation, and recycled for further dehydrogenation. Any stable hydrocarbon boiling in the C₈ aromatics range that is present is substantially unaffected and is not removed in the distillation to separate the residual ethylbenzene from the styrene produced, but a portion remains with the ethylbenzene fraction and thereby tends to build up in concentration therein and a portion remains with the styrene tending to increase the ethylbenzene content to further reduce the styrene purity, thereby reducing the quality of the styrene to below commercial acceptability as described above. Accordingly, the prior attempts to separate ethylbenzene from a C₈ aromatics fraction by a distillation of any character, resulted in such high impurity contents as to render the ethylbenzene useless for styrene production.

The separation of ethylbenzene in adequate degree of purity from a C₈ aromatics fraction is made possible by the present superdistillation only because substantially all stable non-aromatic hydrocarbon boiling in the C₈ aromatics range of about 130 to 140° C., and initially in quantity above about 0.3%, have been removed before that superdistillation is applied. The method of removing such stable hydrocarbon impurities, usually non-aromatics, according to the present invention, comprises extracting the aromatics with a polar type solvent from the mixed hydrocarbon feed stock containing a recoverable quantity of ethylbenzene, usually along with other aromatics. Such polar type solvent is characterized by having a relative selectivity in its solvent effect upon the feed stock hydrocarbon tending to dissolve more aromatics than non-aromatics. In usual operation the solvent to feed ratio may vary from 30 to 5:1.

During the extraction a continuous recycle of lower boiling hydrocarbon, boiling below the C₈ aromatics extract range, is maintained to pass such recycle through the aromatics rich solvent solution, thereby tending to displace from the extract any high boiling non-aromatic hydrocarbon dissolved in the aromatic extract solution, and substitute therefor the lower molecular weight non-aromatic hydrocarbon of the recycle. The extract solution is then distilled first to flash off dissolved low volatile non-aromatics for recycle to the aromatic rich solvent solution in the extractor. The aromatic hydrocarbon is then stripped from the solvent in a semi-steam distillation, separating a front end fraction containing any remaining quantity of volatile non-aromatics and some aromatics as overhead, also for recycle. Simultaneously a side stream of substantially 100% aromatics is removed from an intermediate portion of the stripping column.

In a subsequent distillation of the pure aromatics there is first separated benzene, then toluene and finally a C₈ fraction containing less than 0.3% and usually sub-

stantially no non-aromatic hydrocarbon. That C₈ fraction is then superdistilled to recover the substantially pure ethylbenzene as further described below.

It is occasionally found in certain virgin petroleum naphtha stocks that the C₈ aromatics fraction contains over 15% of ethylbenzene, and sometimes even as high as 25%. Accordingly, such stocks are useful as feed stock to the extractor when they are available, and while the whole range of the distillate may be used, it will be preferable, before extracting such virgin gasoline, to first separate therefrom a fraction which comprises a concentrate of the C₈-C₉ aromatics.

It is also known that many gasoline conversion products contain ethylbenzene among their C₈ aromatics and such conversion products selected at random from many commercial petroleum conversion processes will average about 11% of ethylbenzene among their C₈ aromatics. Such catalytic conversion products, preferably after fractionating to isolate a concentrate of the C₈-C₉ aromatics, may also comprise a useful feed stock to the extractor of the present invention.

It is found that if a naphtha comprising at least 25% naphthenes boiling in the range of 226-273° F. is catalytically dehydrogenated, large quantities of recoverable ethylbenzene, usually exceeding 15%, are found in the C₈ fraction of the aromatics formed therein and therefore, it is preferred to use as feed stock to the present extractor such catalytically dehydrogenated product.

A full boiling range petroleum naphtha boiling from 100 to about 400° F., typically about 140-175° F. IBP up to about 400° F. EP, may comprise the feed stock to the catalytic dehydrogenator, providing it initially contains at least 25% of naphthenes. The yields of C₈ aromatics in the aromatized product are also favorably affected by adjusting the feed stock to a high content of hydrocarbons containing at least 25% naphthenes boiling in the range of 226-273° F. Hence, the usual practice of this invention is to feed a naphtha to the catalytic dehydrogenator adjusted to have more than 25% of the feed stock composed of hydrocarbon comprising 25% naphthene boiling in this relatively narrow boiling range. It is found according to this preferred practice of this invention that very high, 27-34% yields of ethylbenzene are obtained when the feed stock to the catalytic dehydrogenator is supplemented by adding much more hydrocarbon boiling in the range of 226-273° F. and which comprises 35 to 55% naphthenes.

For purposes of comparing the yields of ethylbenzene available by the present preferred dehydrogenation procedure to increase the yields, to usual practices, two tables compiled by the Petroleum Refining Laboratory of Pennsylvania State University are reproduced. Table A shows ultimate analysis of the C₈ fraction of various straight run naphthas, and Table B shows a similar analysis upon various catalytically converted naphthas:

TABLE A
Relative amounts of C-8 aromatics present in naphthas

Source Naphtha	Straight Run Naphthas ¹								
	B.P., ° O.	Ponca City	East Texas	Bradford	Michigan	Winkler, Texas	Midway, Calif.	Conroe, Texas	Average
Volume percent of total C-8 Aromatics									
C-8 Aromatics:									
Ethylbenzene.....	136.2	18	17	9	15	25	24	8	17
P-xylene.....	138.4	9	13	16	12	39	16	16	17
M-xylene.....	139.1	48	48	56	51	26	38	57	46
O-xylene.....	144.4	25	22	19	22	10	22	19	20
Total.....		100	100	100	100	100	100	100	100

¹ Rossini, F. D., Hair, B. J., Streiff, A. J., Hydrocarbons from Petroleum, ACS Monograph 121, pages 440 and 452.

TABLE B
Catalytic naphthas

Type of Cracking	B.P., °C.	Hydro-Forming	Fixed Bed		Fluid	
			2-Pass	3-Pass	Low Temp.	High Temp.
Reaction Temp., °F.		925	850	875	800	975
Charging Stock		Selected Naphtha	Gas Oil + Heavy Distillate	Hvy. Naph. from 2-Pass	Kerosene	Gas Oil
Volume Percent of Total C-8 Aromatics						
C-8 Aromatics:						
Ethylbenzene	130.2	11	13	9	12	13
P-xylene	138.4	18	10	20	18	20
M-xylene	139.1	47	48	62	45	49
O-xylene	144.4	24	20	10	24	18
Total		100	100	100	100	100

	38E 80 ¹	38H 65 ¹	38K 65 ¹	30Y 82 ¹	36R-Y 66 ¹	Avg. of
Reaction Temp., °F.	975	975	975	1,000	975	
Charging Stock	Light Gas Oil.	Light Gas Oil.	Heavy Gas Oil.	Gas Oil	Gas Oil	10.
Volume Percent of Total C-8 Aromatics						
C-8 Aromatics:						
Ethylbenzene	10	13	9	11	9	11
P-xylene	22	19	15	20	18	19
M-xylene	48	43	44	45	46	47
O-xylene	20	25	32	24	28	23
Total	100	100	100	100	100	100

¹ Vol. percent conversion.

It will be apparent from the data of Table A that there are some virgin naphthas which naturally contain usefully recoverable quantities of ethylbenzene and some contain relatively high quantities of ethylbenzene in the C-8 fraction whereby such is even more valuably recovered by the present method. With respect to data represented in Table B it is apparent that ethylbenzene available in the C₈ fraction of catalytic conversion stocks by any of the commonly practiced conversion methods is much lower than in Table A, the highest being only 13% of the C₈ fraction, and the average, only 11%, but these too may be usefully recovered. The yield of ethylbenzene by the preferred practice of the present invention may exceed the best of any available virgin or general catalytically produced gasoline stocks.

Accordingly, it is the preferred practice of this invention to aromatize a narrow B.P. range high naphthenic naphtha fraction by catalytic dehydrogenation. The aromatization or dehydrogenation comprises passing the naphtha over a dehydrogenation catalyst, typically a platinum containing catalyst, at a temperature in the range of about 825-975° F. and at a pressure in the range of about 200-500 p.s.i.g. in the presence of at least 4 to 12 mols, preferably 6 to 8 mols of hydrogen per mol of hydrocarbon fed to the unit. The catalytic dehydrogenator comprises several catalytic contact chambers in which dehydrogenation catalyst is distributed for optimum contact with the hydrocarbon vapors and hydrogen mixture, the apparatus providing means for re-heating the vapors at intermediate points between contact chambers to maintain the reaction conditions, there being several, such as 3 to 6 catalytic contact chambers in a dehydrogenation assembly.

The dehydrogenation yield comprises about 75-90 wt. percent of the feed stock, the other products formed comprising some 4-6 wt. percent of hydrogen gas, and

the balance, gases and light liquids separated in a stabilizer. The reaction product after stabilizing and splitting to remove lower volatiles contains at least 30% of aromatic hydrocarbons and usually ranges from about 40 to 60% before solvent separation.

The catalytic dehydrogenation product is stabilized to remove the volatile material which boils substantially below the C₆ aromatics, the product being generally fractionated to an initial boiling point of about 140-155° F. Thereafter the stabilized product is extracted with a polar type solvent in which the solvent tends to dissolve greater quantities of aromatics than non-aromatics.

The character of the solvent may vary widely and includes such typical solvents as lower alkylene glycols such as ethylene, propylene or butylene glycols, lower alkylene glycolethers such as diethylene glycol and dipropylene glycol, furfural, phenol, liquid sulfur dioxide, liquid ammonia, nitrobenzene, aromatic amines such as aniline or toluidine, lower alkyl (1-6 carbon atom) primary, secondary and tertiary amines, and corresponding lower alkanol amines such as tri methyl amine, di ethyl amine, di butyl amine, di ethanol amine, tri ethanol amine and the like, and other polar solvents known in the petroleum extraction art, as well as mixtures thereof, may be used as the solvent. Generally the solvent is modified to impart a small water content for purposes of adjusting its selectivity, primarily to reduce its solvent power for non-aromatic hydrocarbon.

The solvent extraction is usually operated with continuous countercurrent flow of hydrocarbon to be extracted and solvent, with aromatic rich solvent being withdrawn from one end of the extractor and raffinate at the other. A continuous displacement from the extract of high boiling non-aromatic hydrocarbon by lower boiling non-aromatic hydrocarbon is effected by continuously introducing low boiling non-aromatic hydrocarbon into

the extract. The principle here followed to effect a desirable extraction of the aromatic hydrocarbon is based upon the fact that, whatever may be the absolute solubility of non-aromatics in the solvent solution of extracted aromatics, that solvent solution of aromatics has a greater solvent power for non-aromatic hydrocarbon of lower molecular weight than for similar non-aromatic hydrocarbon of higher molecular weight. By continuously passing more volatile lower molecular weight hydrocarbon into the solvent solution of aromatics, any higher molecular weight higher boiling non-aromatic hydrocarbon tends to be displaced from the extract solution into the raffinate and be replaced by the lower boiling non-aromatic hydrocarbon. Thus, the extract solution of aromatics in the polar solvent obtained from this extraction has its non-aromatic content of hydrocarbon composed substantially entirely of low boiling hydrocarbon. In operation of this extraction the low boiling hydrocarbon will be selected to boil below the C₈ aromatics range, and, to aid in practical economical recovery of other aromatics, even below the C₈ aromatics. The total hydrocarbon content is thereafter stripped from the solvent by distillation, both aromatic and non-aromatic hydrocarbon, and because of the substantial difference in boiling points the more volatile lower boiling non-aromatic hydrocarbon may readily be separated from the aromatics. The low boiling hydrocarbon usually boils below 140° C.

In a preferred procedure, a lower alkylene glycoether, such as diethylene glycol or dipropylene glycol, and usually mixtures with a small quantity of water are used as the selective polar type solvent. The solvent is contacted countercurrently with the feed in usual ratio of 30 to 5 parts, preferably 10 to 15 parts, of solvent to 1 part by volume of hydrocarbon feed to be extracted. Obviously any higher ratio could be used with corresponding loss of economy in the process. Such solvent is preferred because it allows the extraction operations to be carried out at substantially raised temperatures and pressures for optimum efficiency. It allows easier separation of the hydrocarbon from the solvent, the more volatile non-aromatics by flashing, and the aromatics in a subsequently applied semi-steam type of stripping with good heat economy. The pure aromatics are readily taken off of a stripping column as a side stream from an intermediate position of the stripping column with any front end content of more volatile non-aromatic hydrocarbon passing overhead.

It is preferred, for ready volatilization of the non-aromatics from the aromatic extract hydrocarbon, to use as non-aromatic displacement feed, a low volatile substantially saturated lower paraffin hydrocarbon, predominantly C₅ paraffins or a C₅ fraction which may contain minor quantities up to about 20% of C₄ and C₆ paraffins, and as a typical C₅ fraction, the feed for displacement to the extractor will usually contain some of both. Such low boiling non-aromatics after separation from the aromatics is recycled to the extractor for continuously displacing heavier non-aromatics from the extract into the raffinate. The total non-aromatic recycle may vary widely from about 1 to 20 volume percent per volume of the extract solution, usually 1 to 5%. Since that volatile non-aromatic hydrocarbon distillate which dissolves in the aromatic solvent solution may be recovered simultaneously with the stripping of the aromatics from the solvent in a stripping column, with the aromatics taken off as a side stream, the stripping in the column may be adjusted to take along with the non-aromatic overhead some 5-10% aromatics. Thereby the side stream aromatic taken off from the column may comprise substantially 100% pure aromatics, and the small 5-10% quantity of aromatics taken overhead with the more volatile non-aromatics become recycled and continuously recovered with the extract in the extractor.

In recycling of the low volatile substantially non-aro-

matic fraction, it is preferred to pass the same upwardly into the bottom of a continuously descending extract solution formed in a vertical column, from which the raffinate is removed at the top, whereby the non-aromatics introduced into the aromatics rich solution act as a continuous wash of the aromatic rich extract and displaces the high boiling non-aromatics upwardly into the column.

While the present invention is directed primarily to production of substantially pure ethylbenzene, inasmuch as the aromatic fraction produced is substantially pure aromatics, it is desirable, for over-all economy of the process, to separate C₆ and C₇ aromatics in separate preliminary distillations, and then separate a pure C₈ fraction from the residual C₈ and higher aromatics. For this purpose the purely aromatic extract, after clay treatment to remove trace quantities of color forming impurities, is fractionated to separate benzene first, then toluene and then fractionated to separate the C₈ fraction from the C₈+ bottoms. Hence, this preliminary fractionation is carried out under narrow boiling point range conditions, thereby to obtain a higher degree of purity for each of these C₆ and C₇ components. For instance, a benzene distillation column is used having at least 12 stages or plates, preferably about 35 to 45 stages and operated with a minimum reflux ratio of at least 1.3:1, preferably about 5 to 7:1, to remove the benzene. In such distillation benzene of 0.884 sp. gr. at 60° F. with a distillation range of 0.5 to 1° C. and a freezing point in the range of 5.3 to 5.45° C., is produced.

In a similar manner toluene may be distilled from the residue of the benzene distillation by distilling in a column having more than 14 stages or plates, preferably from about 35 to 45 stages or plates, operated with a reflux ratio of at least 1.0:1, preferably from about 2.0 to 4.0:1. The toluene thereby produced as overhead may have a boiling point range of 0.5 to 1° C. and a sp. gr. at 60° F. of 0.872. It will be apparent with these fine distillations that both benzene and toluene may be recovered in a reagent grade of purity greatly enhancing the economy of this process.

Either the total C₈ plus residue of the toluene distillation, or a C₈ fraction immediately distilled therefrom, is superdistilled in a column of at least 150 stages or plates, preferably 200-400 stages with a reflux ratio of at least 40:1, preferably 60-150:1 thereby to produce ethylbenzene as an overhead having at least the 99% purity as stated above. If the total C₈ plus residue is superdistilled, the bottoms residue of that superdistillation will consist of residual C₈ (mixed xylenes substantially free of ethylbenzene) and C₈+ aromatics. In this procedure the residue of such superdistillation consisting of xylene isomer and C₈+ aromatics may be returned to a xylene distillation column from which the isomeric mixture of pure xylenes may be separated from the C₈+ hydrocarbon.

As an alternate procedure the bottoms or residuum of the toluene distillation may be first distilled in a wide boiling range of 4-10° C. merely to separate in an ordinary distillation the C₈ aromatics from the C₈+ and, thereafter, this wide, 4-10° C. boiling range C₈ overhead fraction may be superdistilled.

Within the limits of minimum distillation stages and reflux ratio stated for the superdistillation, ethylbenzene may be separated from the C₈ aromatics mixture, if the stable non-aromatic hydrocarbon content in the C₈ boiling range is less than 0.3%, in purity of at least 99%. In preferred ranges of conditions given, that is, with more than 200 stages and a reflux ratio of more than 60 to 1, the ethylbenzene obtained has a purity of 99.995%.

The invention is further described with reference to

a specific embodiment illustrated in the drawings, where-in:

Fig. 1 illustrates diagrammatically a feed preparation section,

Fig. 2 illustrates a catalytic dehydrogenation-aromatizer unit,

Fig. 3 illustrates an extraction section,

Fig. 4 illustrates a benzene, toluene and mixed xylene distillation unit, and

Fig. 5 illustrates a super-distillation unit to separate ethylbenzene.

A raw feed stock to be catalytically dehydrogenated to form aromatics therein may be first separated into a naphtha boiling in the range of 100 to 400° F., preferably a narrower boiling point range high naphthalene naphtha of approximately C₆-C₉ hydrocarbon. The formation of such feed stock is illustrated in the feed preparation section Fig. 1. For this purpose, a wider boiling range naphtha, which may be a virgin gasoline or a re-run gasoline, preferably highly naphthenic or of gasolines blended to include a substantial quantity of naphthenic hydrocarbon, is drawn by pump 10 from inlet line 12, and passed by way of line 14 and a heat exchanger 16, to a prefractionator column 18, in which the more volatile ends boiling below 100° F., and usually below the desired initial boiling point feed stock, preferably below the range of 140-175° F., are removed. These light volatile vapors pass overhead of the column 18 through line 20, are cooled to condense a substantial portion to liquid in heat exchanger 22, and then are sent to surge drum 24 from which uncondensed gases are removed through line 26. The condensed liquid is withdrawn through line 28 by pump 30, and part of the liquid is returned by way of line 32 to the top of the prefractionator column 18 as reflux, and the remaining portion is sent to storage via a stabilizer (not shown) through line 34.

A portion of the prefractionator bottoms are withdrawn through line 36, by pump 38 and sent to the center of a charge splitter fractionating column 40, by way of line 42. Another portion of the prefractionator bottoms are withdrawn through line 44 by pump 46 and passed through a reboiler 48 by way of line 50, and returned as a hot vaporous mixture to the bottom of the prefractionator column, by way of line 52.

The charge splitter column 40 is operated to pass overhead vapors by way of line 54 at a temperature boiling in the useful feed stock fraction range, that is, below the end point of about 400° F. The desired overhead vapors are condensed to liquid by heat exchanger 56, passing to surge drum 58, from which it is withdrawn by pump 60 by way of line 62, and passed through line 64. The distillate in line 64 is divided, a portion being returned by way of line 66 to the top of the charge splitter column 40 as reflux, and the remainder sent through line 68 as the desired raw feed stock to be fed to the catalytic dehydrogenation unit illustrated in Fig. 2.

The charge splitter bottoms are withdrawn from the bottom of the column 40, a portion being drawn through line 72, by pump 74, and sent through heat exchanger 16, by way of line 76, and then through a cooler 78, finally passing out of the system, such as to storage, by way of line 80. Another portion of the bottoms drawn through line 70 by pump 82 is passed through reboiler 48, by way of line 84, and returned to the lower end of charge splitter column 40 by way of line 86 as a hot vaporous mixture to effect the distillation in column 40.

The charge formed passing through line 68 has been adjusted to the boiling point range of 100 to 400° F., preferably a narrower range such as 150 to 310° F. It will contain at least 25% of naphthenes, preferably substantially higher, up to about 60%. It may contain a few percent of aromatics, usually not more than 15%,

and the remainder is substantially paraffins. The following table illustrates a useful range as well as a practical preferred range of feed stock characteristics:

TABLE C
Feed stock to catalytic dehydrogenator

	Useful Range	Preferred Range
Gravity, °API at 60° F.	58-60	58-60
Initial Boiling Pt., °F.	100-175	150-170
10% °F.	160-200	170-190
50% °F.	210-300	210-220
90% °F.	240-350	240-250
End Point, °F.	285-400	285-310
Vol. Percent Paraffins	25-75	43-55
Vol. Percent Naphthenes	25-60	35-55
Vol. Percent Aromatic	0-15	8-13

Of this feed stock, the hydrocarbon that typically forms the benzene in the catalytic dehydrogenation product boils in the range of 150-185° F.; the hydrocarbon which forms toluene boils in the range of 185 to 226° F.; hydrocarbon which forms ethylbenzene and isomeric xylenes boil in the range of 226-273° F.; and the hydrocarbon which forms C₈+ aromatics boils in the range of 273-400° F. For present purposes, to form ethylbenzene, it will be apparent that the feed stock has as its preferred components, naphthenic hydrocarbon boiling in the range of 226 to 273° F. Thus, the feed stock passing through line 68 in the feed preparation section, may have been adjusted to the boiling range of 226 to 273° F., or the wider range feed stock such as 100 to 400° F., as described in the operation of Fig. 1 may be used; or this wide boiling range stock may be further enriched with naphthenic hydrocarbon boiling in the range of 226 to 273° F. It is accordingly possible not only to produce the high ethylbenzene content C₈ aromatic fraction by catalytic dehydrogenation of a selected feed stock, but also control the quantity and type of other aromatics that may be produced simultaneously as by-product for enhancing over-all economy of the process by judicious enrichment of the feed stock with desired boiling range naphthenic hydrocarbon.

Referring to Fig. 2, the selected raw feed stock from line 68, under pressure of pump 88, passes through line 90 together with hydrogen from line 102 supplied in proportion of from 4-12 mols, preferably 6 to 8 mols, of hydrogen per mol of hydrocarbon, through heat exchanger 100 to heater 104 by way of line 106. The heater 104 heats the hydrocarbon to the range of about 850-975° F., preferably 910-930° F., to a pressure of 200-500 p.s.i.g., preferably 420-460 p.s.i.g., and the hot vaporous charge is passed by way of line 108, to the first reactor 110, in which the vaporized charge is contacted with a dehydrogenation catalyst, usually platinum. The reaction is endothermic, the charge being cooled substantially as the product becomes dehydrogenated to form aromatics. The vapors are withdrawn from the bottom of the reactor 110 through line 112 and sent to reheater 114, returning after reheating to the desired reaction temperature to a second reactor 116, by way of line 118. The second stage reaction product withdrawn from the bottom of reactor 116 is again passed to reheat 114, by way of line 120, and returned after reheating to the top of the third reactor 122, by way of line 124. The third stage reaction mixture withdrawn from the bottom of reactor 122, is again heated in reheat 114, by way of line 126 and sent to the fourth stage reactor 128, by way of line 130.

The fourth stage reaction mixture withdrawn from the bottom of reactor 128, by way of line 132, is sent through heat exchanger reboiler 134 and then through heat exchanger 100, by way of line 136, is cooled in a second heat exchanger 138 to condense liquids and sent to a gas and liquid separator 140, by way of line 142. A portion

of the uncondensed vapors, mostly hydrogen, are withdrawn from the system through vapor line 144 and a remaining portion sent to a compressor 146 by way of line 148, to recompress the gases, mostly hydrogen, to reaction pressure of about 200 to 500 p.s.i.g., preferably 420 to 460 p.s.i.g., returning the same to the raw incoming feed stock, passing through line 90, by way of line 102.

The condensed liquid reaction product is withdrawn from separator 140, by way of line 150, passing through heat exchanger 152 and thence, by way of line 154, is passed to an intermediate point in a stabilizer column 156. In the stabilizer column, overhead vapors comprising volatile hydrocarbon boiling below the approximate range of 200 to 210° F., under a pressure of 150-200 p.s.i.g. are taken off through line 158, cooled substantially to condense a substantial portion to liquid in cooler 160, and then separated from uncondensed gases in the surge drum 162, the vapors being withdrawn through line 164 by way of pressure regulating valve 163. The liquid is withdrawn from surge drum 162 by pump 166, by way of line 168, and a portion is sent to the top of the stabilizer column as reflux by way of line 170, and a portion is withdrawn as light overhead distillate and sent to storage by way of line 172. The aromatized bottoms from the stabilizer column 156 are withdrawn by way of line 174, and a portion is sent by way of line 176 to reboiler 134 and returned as a hot vaporous mixture to the bottom of the stabilizer column through line 178. The remaining portion of stabilizer bottoms from line 174 are passed through heat exchanger 152 and then, after cooling in exchanger 180, are sent to storage by way of line 182.

In the catalytic dehydrogenation aromatizer section 25-60%, usually 45-53%, of the raw feed stock after stabilizing comprises aromatic hydrocarbon. The following Table D illustrates a useful as well as a preferred range of operating conditions in the catalytic dehydrogenation section:

TABLE D
Operating conditions dehydrogenation section

Equipment	Temperature, ° F.		Pressure, p.s.i.g.	
	Useful Range	Preferred Range	Useful Range	Preferred Range
Inlet No. 1 Reactor.....	890-975	910-930	200-500	420-460
Onthet No. 1 Reactor.....	810-926	810-860	-----	-----
Inlet No. 2 Reactor.....	890-975	910-930	-----	-----
Outlet No. 2 Reactor.....	810-925	845-870	-----	-----
Inlet No. 3 Reactor.....	890-975	910-930	-----	-----
Outlet No. 3 Reactor.....	810-925	875-905	-----	-----
Inlet No. 4 Reactor.....	890-975	910-930	-----	-----
Outlet No. 4 Reactor.....	810-950	890-920	150-500	320-380
Separator.....	35-135	80-105	100-450	300-380
Stabilizer Column: Top.....	190-230	200-210	100-250	120-200
	350-450	400-420	100-250	120-200
		Useful Range	Preferred Range	
Hydrogen to Hydrocarbon-Ratio.....			4-12	6-8
Yield:				
Total Dehydrogenation Product, Weight Percent.....			75-90	80-90
Hydrogen Gas, Weight Percent.....			4-6	4-6
Stabilizer O'head Liquid, Wt. Percent.....			5-12	5-12
Stabilizer O'head Gas, Wt. Percent.....			0.2-1.0	0.2-1.0

The catalytic dehydrogenation products obtained under the conditions set forth in Table D have the following characteristics after stabilizing. B.P. range 140-340° F., vol. percent paraffin 35-65, vol. percent naphthalene 3-10, vol. percent aromatic 25-60. The ethylbenzene obtained from the C₈ aromatics contained therein ranges from 27 to 34% of the C₈ fraction. As stated above, similar ethylbenzene containing naphthas from other sources may be

used as feed stock to the extractor. Since this catalytic dehydrogenation produces such high ethylbenzene content in the C₈ aromatics, it is a preferred feed stock to the extractor.

- 5 The preferred extraction unit, here described, is designed for operation at raised temperatures, typically in the range of 220-325° F., preferably in the range of 280-300° F., and pressure in the range of 80 to 135 p.s.i.g., preferably 125-130 p.s.i.g. Under these conditions the lower alkylene glycol ethers are the most useful solvents, and we use, typically, diethylene glycol or dipropylene glycol or mixtures thereof, with small quantities, up to about 12%, preferably 5 to 10%, of water. When other solvents are used the system may be operated at lower or higher temperatures variable with the physical, such as the boiling point characteristics of the particular solvent.
- 10 In operation of such system, as illustrated in Fig. 3, the feed from storage, for example, the stabilized catalytic dehydrogenated product obtained as illustrated in Fig. 2, or other useful ethylbenzene containing feed stock as described, enters the extraction system through line 182 and is passed by pump 188, first through heat exchanger 187 to preheat the feed to a desired extraction temperature,
- 15 such as 280-300° F., and thence, by way of line 186 to some preselected intermediate level of the extractor 184, such as through pipes 190, 192 or 194, and at a pressure such as from about 125 to 130 p.s.i.g. at which the system is operating.
- 20 Hot solvent at a similar temperature and pressure enters the top of extractor 184 through line 196 in preferred ratio of about 10-15 parts of solvent to about 1 part of hydrocarbon feed. Simultaneously a light hydrocarbon reflux, typically a paraffinic refinery cut, is supplied to the bottom of the extractor 184 through line 202, the C₅ hydrocarbon being generally obtained as recycle from the stripper as explained further below. That paraffinic recycle in line 202 is supplied at about 1½ to 4½% of the solvent rate. The solvent and mostly dissolved aromatic hydrocarbon, with some lesser quantity of non-aromatic components, descend through the column as the extraction proceeds, so that an aromatic rich solvent solution concentrates at the bottom of the extractor 184, and an aromatics poor raffinate hydrocarbon ascends to the top of the extractor 184. The aromatics rich solvent solution is continuously washed by the light paraffinic C₅ hydrocarbon recycle from line 202, which tends to displace from the extract solution as a continuous wash, the heavier non-aromatics dissolved therein, replacing the same with the lighter C₅ hydrocarbon. Thus, the extract solution withdrawn from the extractor 184 through line 198 from which higher boiling non-aromatic hydrocarbon has been replaced by the lighter C₅ non-aromatic hydrocarbon of the recycle is substantially aromatic. The raffinate, as produced in the extraction, and taken off overhead through line 200, contains some of the undissolved recycle C₅ hydrocarbon together with the heavier displaced non-aromatic hydrocarbon from the extract, as well as the unextracted hydrocarbon remaining after contact of the raw feed with the solvent. That raffinate may further contain a small quantity of unextracted aromatic hydrocarbon.
- 25 The raffinate in line 200 is passed to a point near the bottom of water wash column 204, and the raffinate hydrocarbon introduced therein rises countercurrently to a supply of wash water introduced near the top of the column 204 by way of line 206. The washed raffinate is withdrawn from a point near the top of column 204 through line 208 and sent to raffinate storage after cooling in a heat exchanger 210. The wash water, together with small quantities of solvent removed from the raffinate, after descending to the bottom of the water wash column 204, is withdrawn through line 212, and sent to the top of an aromatics extract wash column 248, as impelled by a pump 213.
- 30
- 35
- 40
- 45
- 50
- 55
- 60
- 65
- 70

The hot aromatics rich extract solution in the solvent withdrawn from the bottom of extractor 184 through line 198, is first cooled to the range of 215-250° F., preferably 225-240° F., in heat exchanger 220, and then sent by way of line 218 to a point near the top of a solvent stripper section 216 by way of pressure reducing valve 215. In the solvent stripper 216, by reduction of pressures to below about 50 p.s.i.g., preferably to about 10-20 p.s.i.g., the volatile non-aromatic hydrocarbon (dissolved C₅ paraffin) components flash overhead as vapors through line 220, and the unvolatilized solvent solution of aromatics collecting in the bottom of the flashing section 216, are transferred by way of a float controlled valve 219 through line 221 to a point near the top of a solvent stripper section 217.

In the solvent stripper section 217 all of the aromatics and any of the residual non-aromatics which were not removed in the flashing applied in flashing section 216, are stripped from the bottom of the solvent stripper, a portion of the steam being obtained through line 238 by distillation in heat exchanger 220, and another portion from reboiled solvent heated in the boiler 234, and returned to the bottom of the stripper through line 236. Thus, the stripping in effect, is a semi-steam type stripping, obtained by passage of steam into the bottom of the stripper. At the top of the stripper any of the more volatile residual generally non-aromatic C₅ hydrocarbon is first vaporized and then passed overhead through line 223. Some of the more volatile aromatics are also allowed to pass overhead together with a substantial quantity of steam through line 223, and that overhead product in line 223 is rejoined with the non-aromatic hydrocarbon passing through line 220 as originally flashed from the solvent solution, and both components are cooled in heat exchanger 222 to condense them to liquid and passed to accumulator 224.

Since the non-aromatic hydrocarbons are the most volatile they are efficiently removed from the top of the column through line 223 together with about 5-10% of the most volatile aromatics, and the substantially 100% pure aromatic streams may be taken off of the stripper column 217 as a side stream through line 226, together with some steam. This mixture is cooled in heat exchanger 228 to condense the aromatics to liquid and passed to accumulator 230 together with small quantities of steam condensed to water therewith.

A portion of the solvent accumulating in the bottom of the stripper is withdrawn through line 232, passed to reboiler 234 and returned as a vaporous mixture to the bottom of the column through line 236 to supply the heat for stripping, and concentrate the solvent to contain the desired quantity of water. The remainder of the solvent is continuously withdrawn from the bottom of the stripper through line 196 by pump 214 and returned to the top of the extractor.

The accumulator tank 230, in which the stripped aromatics are collected, has the aromatics withdrawn therefrom by a take-off pipe 244, which passes the accumulated aromatics by way of line 250, as impelled by pump 246, to a point near the bottom of a water wash column 248. The aromatic hydrocarbon rises countercurrently in column 248 to water supplied to a point near the top thereof from line 212. The washed aromatics are withdrawn from the top of the water wash column 248 through line 254 for further processing as illustrated in Fig. 4.

Some water accumulating in a sump below the bottom of accumulator 224 is withdrawn through line 240 and sent to line 238 and returned to stripper 217 after first being vaporized to steam in exchanger 220, thereby furnishing additional steam for the semi-steam stripping operation.

The volatile hydrocarbon flashed overhead in flash column 216 and overhead from the top of stripping column 217, by way of line 220 and 223 to comprise mostly

C₅ hydrocarbon with about 5-10% of more volatile aromatics, is removed from accumulator 224 from pump 242, and passed as continuous recycle to the bottom of the extractor 184 by way of line 202. From time to time additional paraffinic C₅ hydrocarbon may be supplied to the system by way of line 259 to pass the same into line 202 as needed.

Any excess water or deficiency of water is withdrawn or supplied to the system by way of line 256 connecting with line 238. Wash water accumulated in the bottom of wash column 248 is withdrawn from the system by way of line 257.

The useful range as well as preferred operating characteristics of the solvent extraction system, illustrated in Fig. 3, are summarized in Table E:

TABLE E
Operating conditions of glycol ether extraction system

	Useful Range	Preferred Range
Extractor Temperature, ° F.....	220-325	280-300
Extractor Pressure, p.s.i.g.....	80-135	125-130
Stripper Bottom Temperature, ° F.....	250-325	280-300
Stripper Top Temperature, ° F.....	215-250	225-240
Stripper Flash Pressure, p.s.i.g.....	0-50	10-20
Stripper Bottom Pressure, p.s.i.g.....	0-25	5-10
Clay Tower Inlet Temp., ° F.....	400-450	425
Clay Tower Inlet Pressure, p.s.i.g.....	100-225	150-200
Clay Tower Outlet Pressure, p.s.i.g.....	90-200	130-170
Recycle composition:		
C ₅ Paraffin.....	70-100	75-90
C ₅ Paraffin.....	0-20	1-10
C ₅ Paraffin.....	0-20	1-10
Aromatic.....	0-10	5-10
Solvent Composition:		
Wt. Percent Water.....	2-12	5-10
Wt. Percent Diethylene glycol.....	65-98	68-95
Wt. Percent Dipropylene glycol.....	0-33	0-25
Raffinate:		
Gravity, ° API at 60° F.....	67-73	67-73
Volume Percent Paraffins.....	80-95	80-95
Volume Percent Naphthenes.....	2-12	0-5
Volume Percent Aromatics.....	0-10	0-3

Referring to Fig. 4, washed solvent free aromatic extract passing through line 254, with or without intermediate storage, is preheated to heat exchanger 260 and further heated by heater 262 and sent through a clay treating tower 264 to remove slight quantities of impurities such as traces of color forming bodies. The clay treated extract leaves the clay tower through line 266 and, after passing through heat exchanger 260, is sent to a benzene distillation column 268. The benzene vapors passing overhead through line 270 are cooled in condenser 272. The condensate accumulates in the surge drum 274 from which it is withdrawn by pump 276, by way of line 278, and a large portion is returned to the top of the column through line 280 as reflux, and a product portion is withdrawn to storage as benzene by way of line 282. For production of reagent grade benzene, a column of at least 12, preferably 35 to 45 stages or plates are used with a minimum reflux ratio of 1.35:1, preferably 5 to 7:1 is used, whereby benzene of a purity of 0.5-1° C. boiling range may be obtained. The benzene distillation column bottoms are withdrawn through line 284, a portion being passed to reboiler 286, and returned to the still after heating through line 288, and a portion sent through line 290, as impelled by a pump 292 and passed to a toluene distillation column 294.

The overhead vapors of the toluene column 294, passing through line 296 are condensed by condenser 298 and accumulated in surge drum 300. A portion of the condensate withdrawn through line 302 by pump 304 is returned to the top of column 294 through line 306 as reflux, and a portion of the toluene product is sent to storage through line 308. Again, by maintaining a minimum reflux ratio of 1.0:1, preferably 2.0-4.0:1, and using a column of at least 14, preferably 35 to 45 stages or plates, a nitration grade toluene having a distillation

range of 1° C. or less may be produced. The toluene column 294 bottoms, withdrawn through line 310 has a portion passed to reboiler 312 and returned to the column through line 314 and a portion is sent to a xylene distillation column 316, by way of line 318; or alternatively is sent by way of by-pass line 319 directly to superdistillation of Fig. 5 described below.

The C₈ vapors taken overhead through line 320 from the column 316 in a temperature range of 130 to 140° C. are condensed by condenser 322 and passed to surge drum 324, of which a portion is returned by pump 326 to the top of the column 316 by way of line 328 as reflux, and a portion is sent to the superfractionation column Fig. 5 via storage. The C₉ bottoms, withdrawn from the bottom of the xylene column 316 through line 332 has a portion passed through reboiler 334, from which a vaporous mixture is returned through line 336, and a portion is sent by pump 338 to C₉+ bottoms storage by way of line 340 after cooling in exchanger 342. The xylene column 316 has at least 10, preferably 25-35 stages or plates, operating at a reflux ratio of at least 0.15:1, preferably 0.3 to 0.5:1. In this C₈ product distillation, the overhead product has a distillation range of about 4-10° C.

The C₈ overhead, when operating on the narrow range feed stock to the catalytic dehydrogenator, as defined in "Table C" above will comprise about 0-10% toluene, about 27-34% ethylbenzene and the remainder, mixed xylene isomers, of which the metaxylenic is present in predominant portion, about twice that of either of the other xylenes, the para and ortho being in about equal quantities. The mixed C₈ overhead, passed to the ethylbenzene recovery section shown in Fig. 5, is substantially 100% aromatic and usually contains less than 0.05% non-aromatics, well below the critical 0.3% limit. This raw feed stock enters the ethylbenzene recovery system in Fig. 5 through line 330 either directly as leaving the xylene column of Fig. 4 or after intermediate storage.

In an alternate procedure the ethylbenzene may be removed directly by superdistilling the C₈+ bottoms following toluene removal in column 294. Small quantities of toluene boiling much lower than the C₈ aromatics do not interfere with the separation and can be tolerated in reasonable quantities. As being substantially more volatile than either ethylbenzene or styrene, it is simply distilled from the ethylbenzene or a subsequent mixture with styrene. In fact, in the direct dehydrogenation of the ethylbenzene produced, some toluene is usually produced with the styrene so that toluene may be removed even at the later stage, such as when separating undehydrogenated ethylbenzene admixed with styrene in the styrene production. Generally, when operating the toluene column within the preferred limits above stated, the C₈+ fraction removed from the bottom thereof will not contain more than 1-2% of toluene. Of course, a wider range toluene can be distilled from the toluene column, thereby removing all of the toluene from the C₈+ residue; but it is preferred to operate the toluene column to produce a pure toluene product as described, leaving a few percent of toluene in the C₈ plus bottoms. It is possible, accordingly, in an alternate procedure to pass the C₈+ bottoms, directly from the toluene column by way of line 319 to the superdistillation unit of Fig. 5; and the residual C₈ xylene isomers together with bottoms from that superdistillation, may be returned by way of line 409 as feed to the xylene column 316. That feed contains substantially no ethylbenzene, whereby the column 316 removed only the mixed xylene from the C₈+ hydrocarbon. When operating in this manner the xylene as net overhead product of column 316 passing through line 330, are sent by way of line 331 to mixed xylene storage.

As shown in Fig. 5 the C₈, or C₈+ fraction, respectively obtained either from lines 330 or 319, depending upon whether the feed is after or before distillation in xylene column 316, is sent first through heat exchanger

344 wherein the temperature is raised usually sufficient to volatilize some of the C₈ aromatics at any positive feed pressure established by pump 346 to overcome the head pressure of the column at the selected point of entry. Upon heating the heat exchanger 344, the raw feed may be passed to any of several points of either of the distillation columns 348 or 358, by way of line 350, such as to the bottom of the column 348 by way of line 354, to a higher intermediate point through line 356, to a still higher point 352 of column 348, or it may be passed to the center or top of the first column 358 of the series, through line 351 or 353.

The superdistillation in total is effected in a plurality of two, three or more columns, shown here as three columns 348, 358 or 360, using more than 150 plates, such as 200 to 400 plates as preferred, and dividing the same into three columns. Each column as shown, will preferably have from 66 to about 134 plates or stages. The vapors passing overhead from column 358 are introduced at the bottom of the intermediate column 348 by way of line 362, and the vapors passing overhead from column 348 are introduced to the bottom of the column 360 by way of line 364. Simultaneously, the liquid collected as bottoms in column 360 is returned to a point near the top of the preceding column 348 by way of line 366, as impelled by pump 368. The liquid bottoms of column 348 is returned to a point near the top of column 358 by way of line 370, as impelled by pump 372. In this manner one continuous distillation is effected as shown in three separate columns, each having from 66 to 134 plates, whereby the net distilling effect is that of a single column having over 150 and preferably over 200 plates.

The overhead vapors leaving still 360 by way of line 374 are passed through a condenser, preferably an air cooled condenser and to a surge drum 378. Any uncondensed vapors are vented by way of line 380 to a heat exchanger 382 to condense more of the vapors, the cooled liquid and vapor mixture being passed through a vent separator 384 to separate uncondensed vapors, the condensate being returned by way of line 386 to the surge drum 378. Accordingly, the surge drum 378 combined with the vapor condensing unit 382, operates as a refluxing condenser to condense vapors for the surge drum and return the same as condensed liquid to the drum 378 in relatively small quantities, whereby the liquified distillate in drum 378 is maintained as liquid, but only slightly below its boiling point. The hot liquid is withdrawn from the drum 378 by pump 388 by way of line 390 and a large portion at least 40 to 1, preferably 60 to 150:1 of the hot liquid is returned to the top of the final distillation column 360 by way of line 392, as reflux, and a portion passes by way of line 394, through cooler 396, and thence to ethylbenzene storage by way of line 398.

The liquid bottoms from the first column 358 are withdrawn through line 400 as impelled by pump 402, and a portion passes by way of line 404 through heat exchanger 344 and, after cooling further in cooler 406, is withdrawn by way of line 408. Another portion of the bottoms of column 358 in line 404 is passed through line 410 and thence into a reboiler 412, and the hot vaporous reboiler mixture is returned to the lower end of still 358 by way of line 414. In operation of this section, the heated charge introduced to a selected point of one of the columns, such as the mid-point of column 348 under pressure of pump 346, after mixture with vapors also introduced to the bottom from line 362 produced by reboiler 412, will produce liquid bottoms in line 370 which is returned to the top of column 358 as reflux. The bottoms of column 358 after being reboiled in boiler 412 are returned to the bottom of column 358 as a vaporous mixture at a temperature sufficient to volatilize ethylbenzene. The liquid at the bottom of column 360 in similar manner is pumped to the top of

column 348 by pump 368. Finally the hot condensed overhead is returned in part to the top of column 360 according to the critical reflux ratio exceeding 40:1.

Where the raw feed enters the system of Fig. 5 by way of line 330 after removal of C₈+ bottoms in column 316, the bottoms product in line 408 consists of mixed xylenes and may be sent to storage as relatively pure xylenes. Where the feed enters through line 319 as the bottoms product of the toluene column 294, then the product in line 408 is returned to the xylene column 316 by way of line 409 to separate pure mixed xylenes as overhead from the C₈+, which are then sent to storage by way of line 331.

The following examples illustrate the practice of this invention:

Example I.—A naphthenic feed stock is stabilized as described by Fig. 1 to a boiling point range of 156-300° F. The stock has a 10% boiling point of 180° F., a 50% boiling point of 212° F. and a 90% boiling point of 244° F. and produces 50% over at 212° F., the naphtha analyzing 48% paraffins, 42% naphthenes of which 31% boiled above 226° F., and 10% aromatics. It is passed to a first reactor of a series of four containing platinum suspended on a carrier at a temperature of 915° F. and pressure of 430 p.s.i.g. with a hydrogen to hydrocarbon ratio of 7.5 to 1 molar. It was continuously reheated in passage through the series of reactors, each time to the initial temperature of 915° F., the final outlet temperature being 895° F. and the pressure 325 p.s.i.g. It was stabilized in the stabilizer as illustrated in Fig. 2, the top temperature being maintained at 205° F. and the bottom at 415° F. at a pressure of 160 p.s.i.g. The total catalytic dehydrogenation product yield was 87.5% together with 5 weight percent hydrogen gas and 7.5 percent of gas and liquid stabilizer overhead. The product comprised 45% paraffins, 6% naphthene, and 49% aromatics. It was sent to an extractor system illustrated in Fig. 3, operating in a ratio of 12 parts of solvent to 1 part of hydrocarbon feed with a recycle of 0.35 part of recycle consisting of 90 vol. percent C₅ paraffin, 7 vol. percent aromatics, 1 vol. percent C₄ paraffin and 2 vol. percent C₆ paraffin. The solvent composition consisted of 7% water, 73% diethylene glycol and 20% dipropylene glycol by volume. The raffinate composition was 85% paraffin, 9% naphthene and 6% aromatics. The stripped aromatics was washed with water and clay treated at 425° F. It was then distilled in a benzene column having 40 plates operating at a reflux ratio of 7 to 1 to produce benzene having a distillation range of 0.7° C., a freezing point of 5.39° C. and sp. gr. at 60° F. of 0.884. The bottoms of the benzene distillation were distilled in a toluene column having a reflux ratio of 2.7 to 1 to produce toluene having a distillation range of 0.8° C. and sp. gr. at 60° F. of 0.872. The bottoms of the toluene column were sent to a xylene column having 30 plates operating at a reflux ratio of 0.4 to 1 to produce mixed C₈ aromatics having a boiling point range of 6° C. The C₈ aromatics fraction taken overhead analyzed 1.5% toluene, 28.8% ethylbenzene, 16.0% p-xylene, 37.3% m-xylene and 16.4% o-xylene by weight with no analyzable quantity of non-aromatic hydrocarbon boiling in the range of 130-140° F. The C₈ fraction was then sent to a three column still for superdistillation as illustrated in Fig. 5, each column having 130 plates or a total of 390, and distilled at a reflux ratio of 87 to 1. The overhead product consisted of pure ethylbenzene containing 4.5% toluene. That toluene did not need to be removed, but the product was directly useful for styrene production. In a further distillation merely to remove toluene, the residual ethylbenzene recovered was 99.995% pure.

Example II.—A naphthenic feed stock is adjusted to a boiling range of 226-273° F. and analyzed to contain 58% naphthenes, 7% aromatics and 35% paraffins. It

is catalytically dehydrogenated as illustrated in Fig. 2 at an average inlet temperature of 930° F. and a pressure of 445 p.s.i.g. with a hydrogen to hydrocarbon ratio of 8.0 to 1. It was continuously reheated in passage through the series of reactors to the initial temperature and had a final outlet temperature of 905° F. at a pressure of 334 p.s.i.g. The yield was 86%, the balance being light overhead liquid gases and hydrogen. The product comprises 59.5% aromatics, 8% naphthenes and the balance paraffins. The extracted aromatics as illustrated in Fig. 3 after removal of benzene and toluene to form a 5° C. boiling point range C₈ aromatics fraction was superdistilled with a yield of 33% of ethylbenzene having a purity of 99.992% based upon the C₈ aromatics after removal of toluene.

Example III.—The method of Example I was repeated under exactly the same conditions except that the feed stock to the extraction unit consisted of a virgin gasoline fraction obtained from an aromatic base oil having a boiling point range of 140-340° F. The ethylbenzene obtained in the final superdistillation consisted of 15% of the total C₈ aromatics fed to the still, and after further removal of the toluene, the ethylbenzene had a purity of 99.995%.

Example IV.—The conditions of Example I were repeated using as feed stock a cracked gasoline reacted at 850° F. in two passes over an alumina catalyst. It was fractionated to the same boiling point range as in Example II and extracted, all conditions being the same throughout as in Example I. 13% of the C₈ fraction fed to a superdistillation unit was recovered as ethylbenzene having a purity of 99.990% after further removal of toluene.

Thus, as herein set forth in detail, ethylbenzene may be commercially obtained from aromatized, preferably a catalytically dehydrogenated naphtha having at least 25% naphthene content in the raw feed stock, using a ratio of at least 4 to 12 times the hydrocarbon content of hydrogen to produce an aromatized product containing from 40-60% aromatics. The C₈ aromatic fraction will contain at least 15% of ethylbenzene which can be recovered in a superdistillation applied in a still comprising over 150 plates at a reflux ratio exceeding 40:1, providing the C₈ aromatic feed is substantially free of stable non-aromatic hydrocarbon boiling in the range of 130 to 140° C. Such pure aromatic fraction becomes practically available by extraction wherein the critical non-aromatics boiling in this range are displaced by lower-boiling non-aromatics. The high content of ethylbenzene in the C₈ fraction obtained from catalytic dehydrogenation is in itself surprising since neither virgin gasolines or other catalytic naphthas generally contain such high quantities of ethylbenzene among the C₈ aromatics as become available following the specific procedure set forth herein. Thus, while ethylbenzene may be distilled from a xylene mixture therewith from any source in the superdistillation hereof, providing the mixture is first freed of any stable non-aromatic hydrocarbon exceeding 0.3 weight percent thereof, the production of ethylbenzene following the preferred aromatizing procedure hereof forms a raw material which contains unusually large economically recoverable quantities.

Thus, any virgin or catalytic naphtha having an economically recoverable quantity of ethylbenzene may, after removing substantially all of the non-aromatics and forming a mixed C₈ aromatics fraction containing the ethylbenzene, have the ethylbenzene separated by this superdistillation. Similarly, aromatizing procedures other than one using a platinum type catalyst, may be used providing the aromatization is performed upon a highly naphthenic feed stock, whereby to produce substantial quantities of ethylbenzene in the C₈ fraction.

Various modifications will occur to those skilled in the art and accordingly, it is intended that the description

herein given be regarded as illustrative and not limiting except as defined in the claims appending hereto.

We claim:

1. The method of separating ethylbenzene from a mixture with xylene isomers contained in a hydrocarbon mixture which contains other hydrocarbon components comprising first forming of said hydrocarbon mixture a concentrate fraction of said C_8 hydrocarbons from which the stable non-aromatic hydrocarbons boiling in the range of 130 to 140° C. contained in said fraction in quantity greater than 0.3% have been removed, and then superdistilling the ethylbenzene from said fraction in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1.

2. The method of separating ethylbenzene from a mixture with xylene isomers contained in a predominantly C_8 hydrocarbon fraction comprising first removing stable non-aromatic hydrocarbons boiling in the range of 130 to 140° C. contained in said fraction in quantity greater than 0.3% and then superdistilling the ethylbenzene from said C_8 fraction in a distillation column having from about 200 to 400 distillation stages at a reflux ratio in the range of 60-150:1.

3. The method of recovering ethylbenzene contained in a petroleum hydrocarbon naphtha together with other aromatic hydrocarbons, comprising extracting the aromatic hydrocarbon in said naphtha to produce an aromatic extract containing less than 0.3% of stable non-aromatic hydrocarbons therein, distilling said aromatic extract to remove C_8 and C_7 aromatic hydrocarbons and produce a C_8+ fraction containing ethylbenzene and then superdistilling the ethylbenzene from said C_8+ fraction in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1.

4. The method of recovering ethylbenzene contained in a petroleum hydrocarbon naphtha together with other aromatic hydrocarbons comprising extracting said naphtha with a polar solvent having a preferential solubility for aromatic hydrocarbon to form a hydrocarbon solution in said polar solvent in which the aromatic hydrocarbons are predominant, washing said solution with a liquid hydrocarbon having a boiling point range lower than said aromatic hydrocarbon and having a solubility in said solvent greater than the higher boiling non-aromatic hydrocarbon components dissolved in said solvent, thereby displacing said higher boiling non-aromatic hydrocarbons from said solution, separating the aromatic hydrocarbon from other components of said solution by distillation, distilling from said aromatic hydrocarbon mixture a C_8 aromatics fraction having less than 0.3% of stable non-aromatic hydrocarbon therein and then superdistilling said C_8 aromatic fraction to separate ethylbenzene from other C_8 aromatics in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1.

5. The method of producing ethylbenzene comprising catalytically dehydrogenating a petroleum naphtha rich in hydrocarbons having a boiling point in the approximate range of 226-273° F. and comprising at least 25% naphthalene hydrocarbon to form a naphtha containing 40 to 60% of aromatics, extracting the aromatic hydrocarbon from said naphtha under conditions to substantially exclude non-aromatic hydrocarbons exceeding 0.3 volume percent thereof, fractionating the aromatic extract to produce a C_8+ fraction and then superdistilling said fraction in a still having at least 150 distillation stages at a reflux ratio exceeding 40:1 to separate a distillate comprising ethylbenzene containing less than 1% of stable hydrocarbon impurity boiling in the range of 130 to 140° C.

6. The method of producing ethylbenzene comprising catalytically dehydrogenating a high naphthalene petroleum naphtha boiling in the range of 100-400° F. at a temperature in the range of 890-975° F. and a pressure of 200-500 p.s.i.g. in the presence of 4 to 12 mols of

hydrogen per mol of hydrocarbon to produce a dehydrogenation product containing 40-60% of aromatic hydrocarbon, extracting said naphtha with a polar solvent having a preferential solubility for aromatic hydrocarbon to form a hydrocarbon solution in said polar solvent in which the aromatic hydrocarbons predominate, washing said solution with a liquid hydrocarbon having a boiling point range lower than said aromatic hydrocarbon and having a solubility in said solvent greater than the higher boiling non-aromatic hydrocarbon components dissolved in said solvent, thereby displacing said higher boiling non-aromatic hydrocarbons from said solution, separating the aromatic hydrocarbon from the other components of said solution by distillation, distilling from the aromatic hydrocarbon mixture a C_8+ aromatics fraction having less than 0.3% of stable non-aromatic hydrocarbon therein and then superdistilling said C_8+ aromatic fraction to separate ethylbenzene from other C_8 aromatic hydrocarbons in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1.

7. The method of producing ethylbenzene of styrene grade of purity comprising aromatizing a petroleum naphtha to produce an aromatic conversion product containing at least 20 percent of ethylbenzene in the C_8 aromatic components, extracting the aromatic hydrocarbon from the aromatic conversion product by solvent extraction with a relatively polar solvent in a manner to produce an aromatic extract containing not more than 0.3% of non-aromatic hydrocarbons therein, fractionating the extract to produce a C_8+ fraction and superdistilling said C_8+ fraction in a still comprising over 300 distillation stages at a reflux ratio in the range of 60 to 80:1 to separate an ethylbenzene containing less than 1 percent of stable non-aromatic hydrocarbon impurity boiling in the range of 130 to 140° C.

8. The method of producing ethylbenzene comprising catalytically dehydrogenating petroleum naphtha boiling in the range of 100-400° F. and containing at least 25% of naphthalene boiling in the range of 226-273° F. at a temperature in the range of 910-930° F. and a pressure of 420-460 p.s.i.g. in the presence of 6 to 8 mols of hydrogen per mol of hydrocarbon to produce a dehydrogenation product containing 40-60% aromatics, extracting said naphtha with a polar solvent having a preferential solubility for aromatic hydrocarbon to form a hydrocarbon solution in said polar solvent in which the aromatic hydrocarbons predominate, washing said solution with a liquid hydrocarbon having a boiling point range lower than said aromatic hydrocarbon and having a solubility in said solvent greater than the higher boiling non-aromatic hydrocarbon components dissolved in said solvent, thereby displacing said higher boiling non-aromatic hydrocarbons from said solution, separating the aromatic hydrocarbon from said other components of said solution by distillation, distilling from the aromatic hydrocarbon mixture a C_8+ aromatics fraction having less than 0.3% of stable non-aromatic hydrocarbon therein and then superdistilling said C_8+ aromatic fraction to separate ethylbenzene from other C_8 aromatics in a distillation column having from 200 to 400 distillation stages at a reflux ratio in the range of 60-150:1.

9. The method of producing ethylbenzene and other aromatic hydrocarbons in a high degree of purity, comprising catalytically dehydrogenating a petroleum naphtha rich in C_8-C_9 components and containing at least 25 volume percent of naphthalene, to produce a dehydrogenated naphtha comprising 40-60 volume percent of aromatic hydrocarbons, extracting the aromatic hydrocarbon from dehydrogenated naphtha with a polar solvent while displacing non-aromatic hydrocarbons boiling in the range of 130 to 140° C. from said aromatic extract, separating substantially pure benzene from the aromatic extract by fractionally distilling the extract in a column having at least 12 stages at a minimum reflux ratio of 1.35:1, separating substantially pure toluene by fraction-

21

ally distilling the residue of the benzene distillation in a column of at least 14 stages at a minimum reflux ratio of 1.0:1, separating a C₈ fraction from the residue of the toluene distillation, and superdistilling the C₈ fraction in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1 to separate ethylbenzene containing less than 1% of non-aromatic hydrocarbon boiling in the range of 130 to 140° C.

10. The method of recovering ethylbenzene contained in a petroleum hydrocarbon naphtha together with other aromatic hydrocarbons comprising extracting said naphtha with a polar solvent having a preferential solubility for aromatic hydrocarbon to form a hydrocarbon solution in said polar solvent in which the aromatic hydrocarbons predominate, washing said solution with a liquid hydrocarbon having a boiling point range lower than said aromatic hydrocarbon and having a solubility in said solvent greater than the higher boiling non-aromatic hydrocarbon components dissolved in said solvent, thereby displacing said higher boiling non-aromatic hydrocarbons from said solution, separating the aromatic hydrocarbon from other components of said solution to produce a mixture of aromatic hydrocarbons containing less than 0.3% of non-aromatic hydrocarbon components, distilling said aromatic hydrocarbon in a first preliminary distillation in a distillation column having from about 35 to 45 stages at a reflux ratio in the range of about 5-7:1 to separate therefrom substantially pure benzene, distilling the residue in a second preliminary distillation in a distillation column having from about 35 to 45 distillation stages at a reflux ratio in the range of about 2-4:1 to separate substantially pure toluene, and superdistilling the C₈+ residue in a column having at least 150 distillation stages at a minimum reflux ratio of 40:1 to separate ethylbenzene containing less than 1% of stable hydrocarbon impurity boiling in the range of 130 to 140° C.

11. The method of recovering ethylbenzene contained in a petroleum hydrocarbon naphtha together with other aromatic hydrocarbons comprising extracting said naphtha with a polar solvent having a preferential solubility for aromatic hydrocarbon to form a hydrocarbon solution in said polar solvent in which the aromatic hydrocarbons predominate, washing said solution with a liquid hydrocarbon having a boiling point range lower than said aromatic hydrocarbon and having a solubility in said solvent greater than the higher boiling non-aromatic hydrocarbon components dissolved in said solvent, thereby displacing said higher boiling non-aromatic hydrocarbons from said solution, separating the aromatic hydrocarbon from other components of said solution to produce a mixture of aromatic hydrocarbons containing less than 0.3% of non-aromatic hydrocarbon components, distilling said aromatic hydrocarbon in a first preliminary distillation in a distillation column having from about 35 to 45 stages at a reflux ratio in the range of about 5-7:1 to separate therefrom substantially pure benzene, distilling the residue in a second preliminary distillation in a distillation column having from about 35 to 45 distillation stages at a reflux ratio in the range of about 2-4:1 to separate substantially pure toluene, distilling the C₈+ residue in a third preliminary distillation in a column having from 25 to 35 distillation stages at a reflux ratio of about 0.3 to 0.5:1 to separate a C₈ fraction having a boiling point range of about 4 to 10° C., and superdistilling said C₈ fraction in a column having from 200 to 400 distillation stages at a reflux ratio of 60-150:1 to separate a distillate ethylbenzene containing less than 1% of stable hydrocarbon impurity boiling in the range of 130 to 140° C.

12. Method of recovering ethylbenzene contained in a hydrocarbon naphtha including other aromatic hydrocarbons as well as non-aromatic hydrocarbons comprising extracting said naphtha at a temperature in the range of 220-325° F. at a pressure of 80 to 135 p.s.i.g. with a polar solvent comprising a lower alkylene glycol ether 70 75

22

by continuously passing said solvent under said extracting conditions countercurrently in contact with said naphtha in a ratio of 5 to 30 parts of solvent per part of naphtha by volume to produce an aromatics rich extract solution and aromatics poor raffinate, washing said extract solution with liquid C₈ paraffin hydrocarbon whereby higher boiling non-aromatic hydrocarbon components dissolved in said solvent are displaced from said extract solution into said raffinate while being replaced by said C₈ paraffin hydrocarbon, reducing the pressure of said extract solution to flash off dissolved C₈ hydrocarbon components, stripping the aromatic hydrocarbon from the solvent with steam to separate a fraction comprising substantially 100% aromatic hydrocarbon, distilling from said aromatic hydrocarbon mixture a C₈+ aromatics fraction having less than 0.3% of stable non-aromatic hydrocarbons therein boiling in the range of 130-140° C. and then superdistilling said C₈+ aromatic fraction to separate ethylbenzene in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1.

13. The method of distilling ethylbenzene from a mixture with xylene isomers, said mixture being substantially free of non-aromatic hydrocarbon, comprising passing vapors of the said mixture through distillation columns 25 comprising 150 to 400 distillation stages while washing said vapors with condensed liquid in each stage passing countercurrently from stage to stage as reflux, said 150 to 400 stages being separated into a plurality of two to three distillation columns of from 50 to 134 stages each, 30 by passing the liquid mixture to be distilled to an intermediate stage of said 150 to 400 stages, pumping hot condensed liquid from the bottom of the last column to the top of the preceding column through the series of columns as reflux, pumping a portion of the liquid from the bottom of the first column to a reboiler and returning the same as hot vapors to a point near the bottom of the first column, condensing ethylbenzene vapors from the last column to a hot liquid at about its boiling point and returning a portion of the final hot liquid ethylbenzene condensate to the top of the last column as reflux, said columns being operated at a reflux ratio in the range of about 40 to 150:1.

14. Method of recovering ethyl benzene contained in a petroleum hydrocarbon naphtha together with other aromatic hydrocarbons comprising solvent extracting the aromatic hydrocarbons in said naphtha with a polar solvent to produce an aromatic extract containing less than 0.3% of stable non-aromatic hydrocarbons therein, removing a substantial quantity of other C₈-C₈ aromatic hydrocarbon components of said extract to produce a C₈ fraction in which ethyl benzene is relatively concentrated, and superdistilling said concentrated ethyl benzene extract in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1 to produce substantially pure ethyl benzene.

15. Method of recovering ethyl benzene contained in a petroleum hydrocarbon naphtha together with other aromatic hydrocarbons comprising solvent extracting the aromatic hydrocarbons in said naphtha with a polar solvent to produce an aromatic extract containing less than 0.3% of stable non-aromatic hydrocarbons therein, distilling said aromatic extract to remove C₈ and C₉ aromatic hydrocarbons therein and produce a C₈+ fraction containing said ethyl benzene removing a portion of the other aromatic components of said C₈+ fraction to produce a C₈ fraction in which the ethyl benzene is relatively concentrated and superdistilling the ethyl benzene from said concentrated C₈ fraction in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1.

References Cited in the file of this patent

UNITED STATES PATENTS

1,955,246 Link _____ Apr. 17, 1934

(Other references on following page)

23

UNITED STATES PATENTS

2,295,256	Brugma -----	Sept. 8, 1942
2,407,820	Dürrüm -----	Sept. 17, 1946
2,734,930	Schlatter -----	Feb. 14, 1956
2,770,663	Grote -----	Nov. 13, 1956
2,773,918	Stephens -----	Dec. 11, 1956

FOREIGN PATENTS

625,570	Great Britain -----	June 30, 1949
---------	---------------------	---------------

24

OTHER REFERENCES

Rossini et al.: *Pétroleum Réfiner*, volume 21, No. 11, November 1942, pages 73-78.
 Rossini et al.: *Hydrocarbons from Petroleum* (1953),
 Reinhold Publishing Corporation, 330 West 42nd Street,
 New York, New York, page 342.